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The oxidation, reduction, and hydrolyses of silk fibroin

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THE OXIDATION, REDUCTION, AND HYDROLYSES OF SILK FIBROIN

By

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INTRODUCTION

Silk is a protein fiber spun by many varieties of caterpillar as a cocoon for protection while undergoing the change from larva to imago. The practicality of the fibers thus produced for textile purposes depends upon the number of cocoons available, their size, cleanliness, and ease of reeling. The mulberry silkworm, Bombyx mori, has been cultivated for centuries, the optimum conditions for its production of silk are known and applied, and the product is uniform in chemical composition and almost free from mineral impurities. This silk is the mulberry silk of commerce as contrasted with "wild silk", which includes silk derived from all other worms.

The most widely known wild silk is that from Antheraea mylitta, chiefly from the Mirzapu and Benares districts of India (263) and called "Tussah", "Tussur" or "Tussar", names which have become synonymous with all wild silks. Muga is another Indian wild silk, of beautiful fast golden color, and derived from three species of Antheraea, A. assamansis, A. frithii, and A. roylei (112). A third variety of Indian wild silk known as Eri or Eria is derived from Attacus cynthia and Attacus ricini, the oak silkworm and the castor oil silkworm, respectively. (121). Among the Japanese wild silks are Sakusan, from Antheraea pernyi (277), Yama-mai from Antheraea yama-mai (43, 267), and Kuriwata, from Caligula japonica (60, 267). Several wild

silks from China are described in Abderhalden's analyses which follow. Anaphe silk from Africa is coming upon the market in increasing quantities.

Wild silks differ from mulberry silk and differ among themselves in appearance, chemical constitution, and chemical and physical properties. These differences are to be expected, since wild silk may be a mixture of fibers from many varieties of worms grown under different conditions of climate and nutrition. In appearance, the two silks differ markedly. Mulberry silk fibroin is round or oval in cross section, and consists of two brins cemented together by sericin to form one bave. Mulberry fibroin is usually white; some Italian and Japanese varieties are yellowish but easily bleached. Wild silk, on the other hand, is oval, elliptical or flattened in shape, and the fibers are often indented where they cross in the cocoon. Some silks are spirally twisted along the fiber axis (291), while Anaphe silk is round in cross section with regular knots (226). The color of wild silk is usually dark, although it has been found that African wild silkworms produce white silk if reared in the dark (20). The brown color is distributed throughout the fiber and is neither removed during the scouring process nor easily bleached.

There is much variation among the wild silk fibers as to diameter, most of them being thicker than mulberry silk, as shown in Table 1. Anaphe silk is said to be finer than mul-

berry silk (226).

Table 1

The Diameter of the Silk Fiber

Variety	Diameter		Color
	Range millimeter	Most frequent millimeter	
B. mori (291).....	0.009-0.021	0.010	White
B. cynthia (291)...	0.010-0.024	0.014	Brown
B. yama-mai (291)..	0.010-0.045	0.017	Yellowish or colorless
B. faidherbei (291)	0.012-0.034	0.021	Brownish
B. selene (291).....	0.027-0.041	0.034	Colorless, pricked with brown
B. mylitta (291)...	0.014-0.075	0.041	Gray-brown
Caligula japonica (60).....	0.075-0.080		

Wild silks may show a distinct polarization color (291), which aids in distinguishing among them. The silk of Antheraea mylitta and Bombyx mori give similar, although not identical, X-ray diagrams (177); those of Antheraea pernyi and Antheraea yama-mai are alike, but differ slightly from that of mulberry silk (224).

Abderhalden and his students investigated the chemical constitution of silk fibroin and wild silk fibroin by hydrolyzing the silks with 25 per cent sulfuric acid or concentrated hydrochloric acid, and separating and identifying the hydrolytic products. The analyses by these and other workers are shown in Table 2.

Table 2

Amino Acids Resulting from Hydrolysis of S

Investigator	Year	Reference	Variety of Silk	Glycine	Alanine	Ty
				per cent	per cent	pe
Abderhalden	1922	3	Bombyx mori	40.5	25.0	
Abderhalden and Brahm	1909	4	Shantung tussah	14.5	22.0	
Abderhalden and Brossa		6	Niet-ngo-tsam (China)	24.0	18.5	
Abderhalden and Rilliet		10	New-Chwang (China)	19.7	23.8	
Abderhalden and Sington		12	Bengal	30.5	20.0	
Abderhalden and Spack		13	Indian	9.5	24.0	
Suzuki, Yoshimura and Inouye		267	Antheraea pernyi	5.7	4.8	
			Antheraea yamamai	6.3	7.2	
			Caligula japonica	7.7	15.3	
Abderhalden and Schmid	1910	11	Tai-Tsao-Tsam (China)	25.2	18.2	
Abderhalden and Welde		14	Cheefoo	12.5	18.0	
Suwa		266	Haruko	35.0	22.6	
Abderhalden and Inouye	1912	8	Ailanthus (China)	10.5	8.5	
			Tailung (China)	13.0	12.0	
Inouye and Hirasawa	1918	156	Bivoltin	25.4	22.6	
Inouye, Iwaoka and Hirasawa	1920	157	Manchurian Tussah	16.8	11.9	
			Japanese Tussah	12.4	15.3	
Inouye and Ju	1929	155	Lun-Yueh	29.0	19.2	
Abderhalden and Heyns	1931	7	Liao-Ning-Sing	13.0	27.7	
Sah, Ma and Ma	1933	223	Chekiang	35.0	16.5	

Table 2

Amino Acids Resulting from Hydrolysis of Silk

Variety of Silk	Glycine per cent	Alanine per cent	Tyrosine per cent	Serine per cent	Leucine per cent	Aspartic acid per cent
Bombyx mori	40.6	25.0	11.0	1.8	2.5	---
Shantung tussah	14.5	22.0	9.7	1.8	1.0	1.0
Niet-ngo-tsam (China)	24.0	18.5	7.8	1.5	1.2	2.0
New-Chwang (China)	19.7	23.8	9.8	1.0	1.6	2.9
Bengal	30.5	20.0	10.0	1.8	1.2	0.8
Indian	9.5	24.0	9.2	2.0	1.5	2.5
Antheraea pernyi	5.7	4.8	1.4	?	1.2	1.0
Antheraea yamamai	6.3	7.2	2.0	?	1.3	1.0
Caligula japonica	7.7	15.3	5.5	?	8.0	0.2
Tai-Tsao-Tsam (China)	25.2	18.2	7.8	1.2	0.9	2.1
Cheefoo	12.5	18.0	8.5	1.0	1.2	2.0
Haruko	35.0	22.6	9.7	0.7	0.7	1.0
Ailanthus (China)	10.5	8.5	3.3	---	1.0	0.8
Tailung (China)	13.0	12.0	3.6		1.0	1.0
Bivoltin	25.4	22.6	5.7	2.8	0.6	0.1
Manchurian Tussah	16.8	11.9	3.9	0.5	0.2	4.1
Japanese Tussah	12.4	15.3	6.6	0.6	0.3	2.4
Lun-Yueh	29.0	19.2	8.9	1.5	2.9	0.6
Liao-Ning-Sing	13.0	27.7	9.4	1.3	1.6	0.5
Chekiang	35.0	16.5	10.5			

Table 2, Cont'd

Investigator	Year	Reference	Variety of Silk	Glutamic acid per cent	Phenyl alanin per ce
Abderhalden	1922	3	Bombyx mori	---	1.5
Abderhalden and Brahm	1909	4	Shantung Tussah	1.8	1.0
Abderhalden and Brossa		6	Niet-ngo-tsam (China)	3.0	1.0
Abderhalden and Rilliet		10	New-Chwang (China)	1.7	1.2
Abderhalden and Sington		12	Bengal		1.4
Abderhalden and Spack		13	Indian	1.0	0.6
Suzuki, Yoshimura and Inouye		267	Antheraea pernyi		---
			Antheraea yamamai		---
			Caligula japonica	?	
Abderhalden and Schmid	1910	11	Tai-Tsao-Tsam (China)	2.0	1.0
Abderhalden and Welde		14	Cheefoo	2.0	1.0
Suwa		266	Haruko	0.1	1.3
Abderhalden and Inouye	1912	8	Ailanthus (China)	0.8	---
			Tailung (China)	---	---
Inouye and Hirasawa	1918	156	Bivoltin		0.3
Inouye, Iwaoka and Hirasawa	1920	157	Manchurian Tussah		1.2
			Japanese Tussah		0.4
Inouye and Ju	1929	155	Lun-Yueh	1.8	1.0
Abderhalden and Heyns	1931	?	Liao-Ning-Sing	1.1	?

Table 2, Cont'd

Variety of Silk	Glutamic acid per cent	Phenyl-alanine per cent	Proline per cent	Lysine per cent	Arginine per cent	Histidine per cent
Bombyx mori	---	1.5	1.0			
Shantung Tussah	1.8	1.0	2.5			
Niet-ngo-tsam (China)	3.0	1.0	1.2			
New-Chwang (China)	1.7	1.2	1.9			
Bengal		1.4	1.0			
Indian	1.0	0.6	1.0			
Antheraea pernyi		---		?	3.1	2.7
Antheraea yamamai		---		7.4	3.8	1.6
Caligula japonica	?		4.2	2.4	1.7	1.0
Tai-Tsao-Tsam (China)	2.0	1.0	1.0			
Cheefoo	2.0	1.0	2.5			
Haruko	0.1	1.3	0.7			
Ailanthus (China)	0.8	---	0.7			
Tailung (China)	---	---	1.7			
Bivoltin		0.3	0.3			
Manchurian Tussah		1.2	0.2			
Japanese Tussah		0.4	0.3			
Lun-Yueh	1.8	1.0	0.6			
Liao-Ning-Sing	1.1	?	1.5	2.2	0.9	0.9

Anaphe silk was found to yield a large amount of tyrosine, some glycine and alanine, also aspartic and glutamic acids, and traces of leucine and proline: in fact, to be quite similar to the silk of Bombyx mori (2). That from the South American Oeceticus platensis (Berg) was unique in that it gave no tyrosine at all (9).

The relative quantities of amino acids recovered upon hydrolytic cleavage cannot be an accurate measure of the amounts occurring in the protein, for the total recovery is far from complete. The ester method, in the hands of different workers, gives different results with the same silk. Yet in general it may be seen that mulberry silk yields more glycine than alanine, although some wild silks yield the same amount of these amino acids and others yield more alanine than glycine. A larger proportion of tyrosine has been recovered from mulberry silk than from wild silk fibroin.

The distribution of amino acids obtained from silk and wild silk indicates differences in the composition and reactivity of these fibroins. Inouye and Sakamoto (158) state that the distribution of various forms of nitrogen are the same in fibroin, Yama-mai and Tussah, but quite different in Attacus cynthia and Caligula japonica. Values for the nitrogen and ash of mulberry silk are summarized in Table 3. Similar data for wild silk are given in Table 4.

Table 3

The Nitrogen and Ash of Mulberry Silk Fibroin

Investigator	Year	Nitrogen per cent	Ash per cent
Mulder (200)	1837	17.35	0.3
Bolley (42)	1864	17.70	0.71
Cramer (65)	1865	17.35	0.3
		18.89	0.36
		18.40	---
Calvert (53)	1870	17.6	---
Schützenberger and Bourgeois (231)	1875	18.7	---
Königs (24)	1880	----	0.77
Moyret (199)		17.6	---
Persoz (209)	1887	18.0	---
Weyl (289)	1888	17.75	0.56
Vignon and Sisley (277)	1891	19.2	---
Vignon (276)	1892	19.2	---
Richardson (217)	1893	19.00	---
Filsinger (93)	1896	16.23	---
Bell (34)	1897	----	0.35
Gnehm and Bänziger (110)		----	0.55
Steiger and Grünberg (264)		18.33	---
Wardle and Bell (281)		----	0.5
Gianoli and Zappa (108)	1900	19.0	---
Gnehm and Dürsteler(111)	1906	----	0.20
Sisley (241)	1907	18.38	---
Suzuki, Yoshimura and Inouye (267)	1909	18.98	0.63
Abderhalden (1)	1910	17.09	---
Roose (222)		----	1.9
Heermann and Frederking (137)	1914	18.33	---
Herzog and Jancke (141)	1920	----	1.5
Herzog and Kobel (142)	1924	18.07	---
Brigl and Held (47)	1926	19.2	---
Furry (100)	1928	18.46	2.22
Morel and Sisley (198)		18.3	---
Abderhalden and Brockmann (5)	1929	18.58	0.72
Branegan (45)		17.40	---
Forbes and Mack (96)		18.62	---
Jones (167)	1931	18.00	---
Vickery and Block (275)		18.99	---

Table 3, Cont'd.

Fisher (95)	1932	18.52	0.35
Denham and Allen (68)	1933	----	0.03
Dobry-Kurbatow (73)		18.5	----
Goldschmidt, Martin and Heidinger (117)		18.1	----
Walde (280)	1934	18.63	0.23

Table 4

The Nitrogen and Ash of Wild Silk Fibroin

Investigator	Year	Wild silk	Nitrogen per cent	Ash per cent
Bolley (43)	1869	Yama-mai	18.89	---
Bolley and Schoch (44)	1870	Yama-mai	18.89	---
Bastow and Appleyard (32)	1888	Antheraea mylitta	16.85	0.23
Filsinger (93)	1896	Tussah	14.39	----
Abderhalden and Rilliet (10)	1909	New Chwang	----	2.00
Abderhalden and Sington (12)		Bengal	----	0.46
Abderhalden and Spack (13)		Indian	----	1.6
Suzuki, Yoshimura, and Inouye (267)		Antheraea pernyi	18.87	2.92
		Caligula japonica	16.73	3.85
		Yama-mai	17.73	4.73
Abderhalden and Welde (14)	1910	Cheefoo	----	1.5
Abderhalden and Inouye (8)	1912	Tailung	18.50	0.99
Inouye and Hirasawa (156)	1918	Bivoltin	18.19	7.4
Herzog and Jancke (141)	1920	Tussah	----	0.7
Inouye, Iwaoka and Hirasawa (157)		Manchurian	18.44	1.23
		Japanese	18.24	2.00

Table 4, Cont'd.

Srivastava (263).....	1920	Antheraea mylitta	19.57	<1.0
Inouye and Ju (155)..	1930	Lun-Yueh	17.36	1.0
Abderhalden and Heyns(7)	1931	Chinese	17.57	0.82
Colombo (60).....	1932	Caligula japonica	16.76	0.18
Colombo and Jona (62)..	1933	Tussah	18.46	---
Herzog and Weindling (143).....	1933	Tussah	18.10	---

The variations obtained by different workers investigating the same silk may be explained by differences in sampling and methods of degumming and analysis, as well as by differences in the silk which are caused by variations in the diet and health of the worm. In general, the values for nitrogen are slightly higher for silk fibroin than for wild silk fibroin, while the reverse is true of ash, as it is difficult to remove inorganic matter from wild silk by the ordinary process of degumming. The chemical constitutions of silk and wild silk fibroin appear similar although not identical.

The iso-electric range of silk fibroin has been found slightly higher than that of wild silk fibroin. Table 5 summarizes the values reported in the literature:

Table 5

The Isoelectric Range of Fibroin

Investigator	Year	Silk	Isoelectric range pH
Denham and Lonsdale (70)	1924	Mulberry	3.8
Mullin (202)	1926		3.8
Denham and Brash (69)	1927		3.4 - 3.9
		Tussah	3.0 - 3.7
Elöd, Teichmann and Pieper (84)		Mulberry	5.1
Meunier and Rey (196)			4.2
Mullin (203)	1929		3.8
Harris and Johnson (132)	1930		2.0 - 2.4
Hawley and Johnson (133)			1.4 - 2.8
Bitō (40)	1931	Tussah	2.79
		Kuriwata	2.85
Bitō (41)	1932	*Antheraea pernyi*	2.6
		Dictyoplaca japonica	2.8 - 2.92
Harris (128)	1932	Mulberry	2.5
Elöd (83)	1933		3.9
Kaneko and Yamamoto (170)	1934		2.1, 4.15, 5.24

Although the chemical behavior of wild silk has been investigated even less thoroughly than that of mulberry silk fibroin and such descriptions as have been made are in general matters of experience along technological lines, it is desirable to know the behavior of wild silk fibroin toward chemical reagents because this fiber is coming into wide use as spun silk for clothing and upholstery fabrics.

This thesis describes the effect of oxidizing and reducing agents, concentrated acid and alkali, salt and steam upon silk fibroin and the effect of oxidizing and reducing agents,

dilute and concentrated acid and alkali and steam on wild silk fibroin as measured by the weight, nitrogen, and mechanical failure of the residual fibroin.

REVIEW OF LITERATURE

Oxidation of Fibroin

Silk may be exposed to oxidation during its fabrication and its life as a textile, in many bleaching processes, in certain processes of dyeing and printing, and in exposure to atmospheric oxidation.

Oxidizing agents which have been suggested for the bleaching of silk are: hydrogen peroxide (16, 31, 51, 63, 86, 87, 102, 112, 114, 115, 120, 127, 139, 151, 152, 172, 179, 197, 221, 238, 248, 249, 250, 251, 252, 253, 254, 255, 262, 265, 283, 284, 285, 286, 287, 288, 292), sodium peroxide (52, 81, 86, 63, 102, 139, 149, 250, 262, 265, 292), peroxides in general (114, 116, 215, 273), other per-salts, including potassium permanganate (51, 76, 102, 139, 218, 292), sodium perborate (51, 139, 165, 265), percarbonate (51, 49), persulfate (51), chromate (51), as well as aqua regia (51, 229, 290, 292), chlorine (207), bromine (168), hypobromous acid (168), nitrous acid (290), nitric acid and its derivatives (102), ozone (48, 201), and a mixture of ozone and nitrous oxide (201). References to the trade literature giving the actual working conditions are summerized in Table 6.

Table 6

Recipes for Bleaching Silk Fibroin by Oxidation

Oxidizing agent	Investigator	Concentration volume strength	Time hours	Temperature °F.
Hydrogen peroxide	Alexander (16)	3	1 - 2	hot
		3	24	cold
	Alfeld (17)	0.75	6	212
	Cagliostro (51)	3	12 - 48	130
		0.5 - 1	1	190
	Conklin (63)	2 - 3	8 - 12	130
	Emmons (86)	2 - 3	8 - 12	120
	Farrell (91)	3	Several	122
	Hilton (144)	32 per cent by volume on weight silk	1	212
	Hughes (151)	3	---	130
		3	2	to 190
	Hughes (152)	3	---	130
	Jaloux (159)	---	1	115
	Kershaw (172)	1 - 2	16	---
	Lecouteux (178)	0.5	24	cold
				100 - 120
	Moffat (197)	2	Overnight	130, cool
	Pentecost (208)	0.5 - 1	2	to 190
				cold
	Roessler and Hasslacher (221)	2 - 4		----
	Smolens (252)	1	Overnight	175, cool
		1	4	190
		0.5	2	190
		2	6	175
	Weber (286)	1	2	165 - 195
		1.5	2	160
	(287)	1	1	160 - 170
	(288)	1	1	165 - 195
	Wingate (292)	1	8	140 - 160
			2	180

Table 6

Bleaching Silk Fibroin by Oxidation

entration e strength	Time hours	Temperature °F.	Additions
3	1 - 2	hot	Ammonia or borax
3	24	cold	
0.75	6	212	Monopole oil, Prästabitol
3	12 - 48	130	Soap, silicate, ammonia
0.5 - 1	1	190	
2 - 3	8 - 12	130	Soap, silicate
2 - 3	8 - 12	120	Soap, silicate
3	Several	122	Silicate or ammonia
r cent by on weight silk	1	212	Silicate
3	---	130	Ammonia, soap or silicate
3	2	to 190	
3	---	130	Ammonia, borax, magnesia, silicate
---	1	115	Barium peroxide, silicate, glycerol
1 - 2	16	---	Ammonia to pH 10 - 11.
0.5	24	cold	Ammonium perchlorate, hypochlorite, nitrate,
		100 - 120	arsenite, carbonate, oxalate, formate.
2	Overnight	130, cool	---
0.5 - 1	2	to 190	Ammonia, magnesia or silicate
		cold	
2 - 4		---	pH 3 - 6.5
1	Overnight	175, cool	Silicate
1	4	190	
0.5	2	190	Silicate, sulfonated castor oil
2	6	175	Silicate
1	2	165 - 195	Silicate
1.5	2	160	
1	1	160 - 170	
1	1	165 - 195	
1	8	140 - 160	Silicate, sodium phosphate or ammonia
	2	180	

Table 6, Cont'd

Oxidizing agent	Investigator	Concentration per cent	Time hour	Temperatu °F.
Sodium peroxide	Alfeld (17)	4	1	212
	Cagliostro (51)	0.6	---	180
	Conklin (63)	0.6	---	180
	Emmons (86)	0.5	---	---
	Farrell (91)	1	---	180
	Hughes (149)	---	3	190
	Moffat (197)	10*	---	---
	Pentecost (208)	1	---	---
Potassium permanganate	Cagliostro (51)	12	---	---
	Hughes (150)	12	0.25	cold
	(151)	12	---	60
	(152)	12	0.25	60
	Rinoldi (218)	0.3	3 - 4	---
Sodium perborate	Jones (165)	0.5	---	---
Chlorine	Ozanam (207)	---	---	lukewarm
Bromine	Jousselin (168)	2	24	cold
Ozone	Brown (48)	2	6	room temperature
		density		
Aqua regia	Alexander (16)	1.01	---	---
	Cagliostro (51)	1.01	0.25	cold
	Hughes (150)	1.01	---	---
	(151)	1.20	0.25	---
	Pentecost (208)	1.02	0.25	cold

*calculated on weight of fabric.

Table 6, Cont'd

Concentration per cent	Time hour	Temperature °F.	Additions
4	1	212	Ammonia or silicate and Prästabitol
0.6	---	180	Silicate
0.6	---	180	Soap, silicate
0.5	---	---	----
1	---	180	Ammonium phosphate
---	3	190	----
10*	---	---	----
1	---	---	----
12	---	---	
12	0.25	cold	
12	---	60	
12	0.25	60	
0.3	3 - 4	---	Magnesium sulfate, 0.35 per cent
0.5	---	---	
---	---	lukewarm	
2	24	cold	
2	6	room temperature	
density			
1.01	---	---	
1.01	0.25	cold	
1.01	---	---	
1.20	0.25	---	
1.02	0.25	cold	

The oxidizing agents which have been recommended for wild silks are summarized in Table 7. Estey (87) has reported wild silks more resistant than mulberry silk to oxidation.

Although the trade literature abounds in these empirical recipes for the bleaching of silk, there are few quantitative data available on the effect of oxidizing agents on fibroin. Estey (87) noted that prolonged peroxide bleaching injured strength, elasticity and luster of silk, and Pokorný (213) that peroxide bleaching at a high temperature yellowed wild silk.

Pentecost (208) studied the effect of concentration upon the hydrogen peroxide bleaching of wild silk and found that three-volume and one-volume peroxide gave a better bleach than one-half-volume peroxide. In a study of the effect of different alkalies, holding the peroxide concentration constant, he found that sodium silicate gave the best bleach, magnesia and ammonia the next best, and borax the poorest.

Dorée (75) reported that, although satisfactory for wool under certain conditions, the ozone bleach (2 per cent ozone in air saturated with moisture) powerfully attacked silk. The fibers became acid and sticky and dried yellow, harsh and lusterless. Dorée's work is summarized in Table 8.

Table 7

Recipes for Bleaching Wild Silk Fibroin by Oxidation

Oxidizing agent	Investigator	Concentration volume strength	Time hour	Temperature °F.	
Hydrogen peroxide	Alfeld (17)	Twice weight of silk of 3-volume peroxide	4	212	Silica
	Anon. (28)	2	a few	120	Soap,
	Beltzer (35)	6 - 10	4 - 5	30-40	Ammoni
	Cagliostro (51)	0.5	24	room	Ammoni
	Clarou (58)	4	-	80-90	Silica
	Cleve (59)	-	3	cold	
			3	hot	Silica
	Friedman (98)	6 - 10*	-	95	Ammoni
	Garcin (102)	0.5	6 - 8	100-120	(Alkal
	Göhring (112)	1	8 - 9	195	Silicat
	Gütman (126)	-	-	185	Biancol
	Hughes (150)	1	10	cold	
			2	190	Silicat
	Köchlin-Baumgartner (174)	-	5	---	Soap, n
	Matos (185)	3	12	---	Ammonia pH
		10	Dip and age		Ammonia
	Murray (204)	10	-	---	Potassi ium h
		9*	0.75 - 1	212	Silicat
	Penteco st (208)	1	72	---	Ammonia
	Pokorny (213)	10	-	---	(Alkal
	Silbermann (238)	3	12, twice	room	Ammoni chlor
		3	24	room	Ammoni
		10	-	room	Potass ate,
	Weber (287)	1 - 2*	0.75-2.5	185-195	Silica

*per cent by volume.

Table 7

ipes for Bleaching Wild Silk Fibroin by Oxidation

Investigator	Concentration volume strength	Time hour	Temperature °F.	Additions
lfeld (17)	Twice weight of silk of 3-volume peroxide	4	212	Silicate, Prästabitol
Anon. (28)	2	a few	120	Soap, silicate
Beltzer (35)	6 - 10	4 - 5	30-40	Ammonia
Cagliostro (51)	0.5	24	room	Ammonia or borax
Clarou (58)	4	-	80-90	Silicate
Cleve (59)	-	3	cold	
		3	hot	Silicate
Friedman (98)	6 - 10*	-	95	Ammonia
Garcin (102)	0.5	6 - 8	100-120	(Alkaline)
Göhring (112)	1	8 - 9	195	Silicate
Gütman (126)	-	-	185	Biancol
Hughes (150)	1	10	cold	
		2	190	Silicate
Köchlin-Baumgartner (174)	-	5	---	Soap, magnesia
Matos (185)	3	12	---	Ammonia, sodium hydroxide to pH 13.
	10	Dip and age		Ammonia
Murray (204)	10	-	---	Potassium carbonate, ammonium hypochlorite
	9*	0.75 - 1	212	Silicate, glycerol
Pentecost (208)	1	72	---	Ammonia
Pokorny (213)	10	-	---	(Alkaline)
Silbermann (238)	3	12, twice	room	Ammonium carbonate, potassium chlorate and sodium nitrite
	3	24	room	Ammonia, sodium hydroxide
	10	-	room	Potassium or ammonium carbonate, ammonium hypochlorite
Weber (287)	1 - 2*	0.75-2.5	185-195	Silicate

Table 7, Cont'd

Oxidizing agent	Investigator	Concentration per cent	Time hour	Temperature °F.
Sodium peroxide	Anon. (25)	1 - 2	2.5 -2.75	80 - 95
	Cagliostro (51)	0.8	0.75	to 190
		1	6 - 8	140
	Emmons (85)	-	6 - 8	212, cool
	Hughes (150)	1.2*	0.75	cold
			0.75	190
		1	6 - 8	to 190
	(151)	1.2*	0.75	to 190
	Grover-Palmer (121)	-	2	85
			2	120
	Pentecost (208)	0.75	2.75	to 190
Potassium permanganate	Cleve (59)	5*	-	85 -120
	Heinrich (138)	-	-	-
	Hurst (154)	12	4	120
Sodium perborate	Jones (165)	0.5	-	to 150

*calculated on weight of fabric

Table 7, Cont'd

tor	Concentration per cent	Time hour	Temperature °F.	Additions
	1 - 2	2.5 -2.75	80 - 95	Magnesium sulfate
(51)	0.8	0.75	to 190	Magnesium or zinc sulfate
	1	6 - 8	140	Silicate
)	-	6 - 8	212, cool	----
0)	1.2*	0.75	cold	Magnesium sulfate
		0.75	190	
	1	6 - 8	to 190	Silicate
1)	1.2*	0.75	to 190	Magnesium sulfate
mer (121)	-	2	85	
		2	120	Turkey red oil
(208)	0.75	2.75	to 190	Magnesium sulfate
	5*	-	85 -120	----
138)	-	-	-	Magnesium sulfate, or hydrogen peroxide and borax
)	12	4	120	----
)	0.5	-	to 150	Silicate

Table 8

The Ozone Bleach on Silk

Silk	Time	Strength		Elongation	
	hour	gram	per cent	millimeter	per cent
Silk	0	830	100	19.0	100
	00.5	800	96	17.2	91
	1.0	630	76	10.9	57
	3.0	403	49	6.0	32
	6.0	100	12	2.3	12
Spun silk	0	481	100	12.9	100
	0.5	467	97	12.5	97
	1.0	343	71	10.3	80
	3.0	166	35	4.9	38

Oxidizing agents may be applied to silk to oxidize certain dyes: Schroers (230) has recommended perborate in acetic acid solution to supplant air oxidation of certain Indanthrene colors; chromate has been used to oxidize dyes applied to silk in the leuco condition (78) or to discharge indigo-dyed silks when followed by an acid bath and peroxide or percarbonate (164). Nitrous acid has been described as best for applying water-soluble vat dyes to silk (80, 273), at a concentration low enough to prevent yellowing of the silk.

Silk undergoes appreciable deterioration when exposed to certain atmospheric conditions: Harris and Jessup (130) have found that photochemical decomposition of silk is hastened by acid treatment, and Harris has presented evidence that this decomposition is catalyzed by moisture (129); Sommer (260) has studied the effect of weathering upon silk, but without separating the different factors involved in weathering, such as

temperature, light, moisture, oxidation and fumes.

An oxidation of silk resulting in tendered, discolored spots which develop during storage has been attributed to common salt picked up in the dyeing process and elsewhere (242).

Alkaline iodine oxidation of silk has been reported to yield iodoform (148), while hypobromous acid has been found to attack free amino groups in the silk molecule (118), leaving an insoluble product of constant composition (117). Dakin's solution, 0.5 per cent hypochlorous acid, has been found to dissolve silk completely in 36 hours (57), liberating 7.81 per cent of nitrogen (53); Farrell reported that the silk is yellowed before it is destroyed (91). Chloride of lime, in amounts beyond that required for bleaching, has been recommended to soften and improve the luster of Tussah silk (232).

Reduction of Silk Fibroin

Reducing agents are applied to silk as a part of the bleaching operation, in the stripping of dyes and in application of discharge dyes, in the process of weighting, and in attempts to retard the deterioration of weighted silks.

The reducing agents used for bleaching include sulfur dioxide (16, 17, 51, 63, 102, 139, 152, 212, 236, 290), sulfurous acid (76, 51, 212, 229, 139), sodium bisulfite (51), sodium sulfite (76, 139), sodium hydrosulfite (63, 74, 119, 151, 208, 214, 271) and its derivatives (213, 271). The white obtained

by use of these sulfur compounds is not permanent (86) because of the ease of reoxidation especially upon soap or alkaline after-treatments (51).

"Stoving" or the so-called "sulfur bleach" is obtained by hanging damp silk in an air-tight chamber and subjecting it to the action of gaseous sulfur dioxide which dissolves in the water to form sulfurous acid. Although few references are made to the exact details of the stoving process, Hughes (151) and Pentecost (208) recommend the use of one-half pound of sulfur per one thousand cubic feet of space, and five pounds of sulfur per one hundred pounds of silk. Alfeld (17) recommends a twelve-hour treatment for crêpe de Chine.

The sulfurous acid bleach is essentially the same as stoving. Concentrations are seldom specified in the trade literature, although it is possible to make cold solutions as concentrated as 3.5 M sulfurous acid. One to fourteen days' treatment has been recommended (21).

Sodium hydrosulfite is used to bleach Tussah (214) and soupled silk. The silk is steeped in hydrosulfite solution for six hours, washed in water and in dilute acid to remove all traces of zinc (51, 151, 208).

Hydrosulfite is used in dyeing in several different ways: the whole dyebath is reduced before immersion of the silk which is subsequently allowed to oxidize as in indigo dyeing (288a); hydrosulfite (78), sulfite, or thiosulfite (80)

may be made into a paste and used to print reserves upon a fabric which is to be dyed with leuco vat dyes; or the fabric may be dyed in the piece and then discharged in pattern.

The reducing agent sodium bisulfite has been recommended to reduce the alkalinity of the bath in dyeing sulfur colors on silk (273). It has also been used to print unchlorinated silk, in the concentration of 135 grams of bisulfite per kilogram of bath (169).

Certain weighting processes involve the addition of reducing agents to the weighting bath. Formaldehyde has been used to precipitate proteins upon silk for the purpose of increasing its weight (52). Carstanjen (54) has added sulfite and thiosulfates to increase the fixation of zinc salts. Weighted silks may be subjected to an after-treatment with reducing agents as a protective measure, the theory being that upon subsequent exposure to light and atmospheric oxidation these more easily oxidized substances will be oxidized before the fibroin. That many of these substances have the desired effect has been questioned (61, 106, 190, 244), although the list of the substances proposed includes hydroxylamine (36, 37, 38, 39, 90, 125, 145, 227), aldehydes (293) including formaldehyde and formaldehyde-bisulfite addition product (90, 176, 188, 191, 192, 193), sulfites (176), thiocyanate (107, 147, 187, 188, 190, 193, 227, 243, 256), urea (77, 146, 293), thiourea (77, 90, 188, 227, 243, 245, 257, 258), hydro-

quinone (90, 146, 188, 257, 258), guanidine (77), hydrazine and its derivatives (186), ammonium formate (125, 145, 205), ammonium cyanate (125), hydrosulfite (140) and thiosulfate (90, 140).

The wide use of reducing agents in the technology of silk, often in quite concentrated solution and at high temperatures, suggests that silk is quite inert towards reducing agents although their action upon the chemical and mechanical properties of fibroin has not been reported in the literature.

Alkaline Degradation of Fibroin

The literature of the alkaline degradation of mulberry silk fibroin has been reviewed previously (280). The effect of dilute solutions of sodium hydroxide for ten hours at 25°C. and 40°C. and for one hour at 100°C. upon the weight, nitrogen, and mechanical failure of mulberry silk is summarized in Table 9.

Table 9

Effect of Dilute Alkali on Silk Fibroin

Sodium hydroxide	Time	Temperature	Residual silk fibroin			
			Weight	Nitrogen	Breaking strength of wet warp	Elongation at breaking load
normality	hour	°C.	per cent of silk	per cent of silk	pound per inch	per cent
0	10	25	99.8	18.63	40	28
0.2197			98.7	18.40	30	23
0.2570			98.6	18.30	25	20
0.3560			97.4	18.08	20	14
0.5140			95.4	17.67	10	7
0	10	40	99.8	18.54	38	29
0.1000			98.5	18.08	27	19
0.1500					19	13
0.2054			96.3	17.86	14	10
0.2500			94.9	17.52	10	8
0.3560			88.3	16.38	< 1	
0.5000			80.2	14.77	< 1	
0	1	100	98.9	18.24	40	32
0.0452			90.8	16.61	10	10
0.0969			59.7	10.86	< 1	

For the production of special finishes caustic alkali has been used upon mulberry silk as a local degumming agent (27, 162, 163).

Wild silk fibroin has been found to be more slowly attacked by alkali than the fibroin of Bombyx mori (7, 85, 235, 263), a fact which makes possible the use of quite strongly alkaline solutions for degumming wild silks. The following conditions have been recommended as causing no damage to the fiber:

Table 10

The Degumming of Wild Silk

Investigator	Conditions
Silbermann (238)	Silk entered at 40° to 45°C. in 30 per cent sodium carbonate on weight of silk; raised to 85° to 90°C. one-half hour; held at that temperature for one to one and one-half hours.
	Ten per cent sodium carbonate on weight of silk at 50° to 60°C.; a second bath in 30 per cent oleic soap solution at 95°C. for 45 minutes.
Heinrich (138)	One per cent sodium carbonate and ten to twelve per cent soap; silk boiled for two hours. Process repeated.
Emmons (85)	One per cent sodium carbonate or one-half per cent sodium hydroxide at the boil.
Alterhoff (18)	Ten per cent sodium carbonate on weight of silk at 85°C. for one and one-half hours. Then 25 per cent Marseilles soap with 3 per cent sodium carbonate for one and one-half hours.
Murray (for Anaphe silk, 204)	Two per cent sodium carbonate solution for one-half hour, preceeding the bleach.

In bleaching of wild silk, Matos (185) recommends a bath made up to pH = 13 with ammonia and sodium hydroxide, steeping the silk for twelve hours.

Tussah may be differentiated from mulberry silk on the basis of its greater resistance to alkali, silk dissolving in twelve minutes in hot 10 per cent sodium hydroxide, and Tussah requiring fifty minutes for complete solution (32).

Acid Degradation of Silk

The hydrolysis of mulberry silk by acids has been reviewed previously (280) and the effect of dilute solutions of hydrochloric acid for ten hours at 40°C., and for one hour at 100°C. upon the weight, nitrogen and mechanical failure of a plain-woven fabric is summarized in Table 11:

Table 11

Effect of Dilute Acid on Silk Fibroin

Hydrochloric acid	Time	Temperature	Residual silk fibroin			
			Weight	Nitrogen	Breaking strength of wet warp	Elongation at breaking load
normality	hour	°C.	per cent of silk	per cent of silk	pound per inch	per cent
0	10	40	99.9	18.63	38	29
0.3009			99.2	18.64	30	22
0.4115			99.1	18.59	29	21
0.4979			99.2	18.41	27	20
1.0263					13	10
1.2664			97.5	18.30	11	8
2.1216			94.2	17.54	<1	
0	1	100	99.6	18.54	40	32
0.0304			98.5	18.37	32	23
0.0720			97.7	18.30	20	14
0.1019			97.7	18.09	17	13
0.1575			94.5	17.64	9	7
0.1950			95.0	17.49	5	5

Concentrated acids have been used in the technology of silk for the production of crêpe effects under the conditions described in Table 12:

Table 12

The Use of Concentrated Acids on Silk Fibroin

Acid	Density	Temperature °C.	Time minute
Sulfuric (71,72).....	1.375 - 1.400	15 - 37	5 - 15
Hydrochloric (71,72).	1.130 - 1.145	5 - 35	1 - 15
(92)....	1.145 - 1.147	---	1 - 2
Nitric (71, 72).....	1.370 - 1.330	5 - 45	0.5 - 15
o-Phosphoric (71, 72)	1.450 - 1.500	25 - 45	2 - 15

Meta phosphoric, acetic and formic acids of various concentrations have been described as ineffective in shrinking silk, and sulfuric acid as greatly tendering silk (92).

In order to modify its transparency, luster and dyeing properties, inorganic acids, sulfuric acid (sp. gr. 1.455) hydrochloric acid (sp. gr. 1.163) and o-phosphoric (sp. gr. 1.525), together with a protective agent, have been used on silk, at a low temperature (134, 135, 136). Formic acid has also been used to straighten, render compact, and improve the luster of fabrics printed with a resist (237). Concentrations of 60 to 70 per cent (216) and of 80 to 100 per cent for 3 to 10 minutes, with or without the addition of 5 to 10 per cent of glycerol (259), have been recommended. Acetic anhydride, alone or with formic acid or glacial acetic acid, has also been used in a twelve-hour treatment (259). Sulfuric

acid of unspecified concentration has been used as a swelling agent (135).

Wild silk has been shown to be much more slowly attacked by acids than mulberry silk (7, 235, 263). Twenty-five per cent sulfuric acid effects complete hydrolysis, although fuming hydrochloric acid leaves a residue (4). Inouye and his coworkers have reported that hot concentrated hydrochloric acid affects wild silks as described in Table 13.

Table 13

The Effect of Concentrated Hydrochloric Acid upon Wild Silk

Variety of silk	Nitrogen		Silk
	Total	Soluble in acid	Soluble in acid
	per cent	per cent	per cent
Bivoltin species (156)...	18.19	17.19	-----
Antheraea pernyi (267)...	18.87	16.39	92.21
Antheraea yama-mai (267)..	17.73	17.26	97.07
Caligula japonica (267)..	16.73	15.77	88.34

Bastow and Appleyard (32) reported that cold, concentrated hydrochloric acid only partially dissolved the silk of Antheraea mylitta in 48 hours.

The difference in the solubility of the two fibroins in acid has been made the basis of several methods of separation and identification. Bastow and Appleyard (32) found that silk dissolved in five minutes in concentrated nitric acid, while wild silk required ten minutes for solution. A difference in reactivity toward chromic acid has been observed (235, 263);

wild silk was unattacked when boiled for two to three minutes in half-saturated chromic acid, which dissolved silk. Von Höhnel found that two minutes' boiling in hydrochloric acid dissolved Yama-mai (279).

Dilute acid treatment before scouring has been suggested (263, 273) as an aid in removing inorganic substances from wild silk.

Effect of Sodium Chloride on Silk Fibroin

Use of sodium chloride in the technology of silk is avoided if possible (123, 273), although recommended in peroxide bleaching (248) and experimental dyeing (184). Small amounts of common salt have been described as weakening weighted silk (64, 194, 210), especially when allowed to dry in the silk (67) at high temperatures (171). Thomson (273) observed that silk bathing suits tendered when salt water dried in them. It is interesting to note, however, that dyed silk submerged in sea water for ten years on a sunken liner showed no mechanical deterioration, although raw silk, recovered after a two-year submersion in a Canadian river, was slightly impaired in tenacity and winding quality (26).

Sweat has long been thought to cause extensive damage both to silk and weighted silk. Sisley (240, 246) proved that only the sodium chloride present caused discoloration and tendered spots identical to those found in stored silks; the deterioration was greatly influenced by humidity and temperature (109,

183, 246, 247). The salt of saliva and urine produced the same results (194). Many workers subsequently identified crystalline sodium chloride in the so-called "red spots" (109, 166, 189, 239, 240, 242, 246), while Marnas (182) found that discolored spots on inked samples of weighted silk appeared in the order of decreasing concentration of salt in the inks. Other metallic halides, as well as the halogen acids, have been reported to weaken silk (109, 181, 242).

This decomposition of silk has been attributed to oxidation (242), according to the equations,

$$NaCl + H_2O \longrightarrow NaOH + HCl$$

$$2\ HCl + O\ (air) \longrightarrow 2\ H_2O + Cl_2$$

$$Cl_2 + 2\ H_2O \longrightarrow 2\ HCl + O.$$

Additional evidence favoring the oxidation hypothesis has been advanced. Jones and Parr (166) have stated that silk discolored by salt may be restored to normal appearance and strength by washing with reducing agents, and Gianoli (105) has found that silk treated with salt and exposed to light in an atmosphere containing oxygen decreased in elasticity and water-soluble nitrogen, while the same silk exposed to light in an inert atmosphere was not attacked.

Göhring (113) raised the question that salt might not be the sole cause for this decomposition of silk. Georgievics and Müller (278) found ferric iron always present in the damaged spots, although usually present in the ferrous state in other

parts of the fabric, and advanced the theory that iron acts as catalyst for the oxidation. Gianoli (104) suggested that copper was an even better catalyst for the oxidation, and Meister (189) found copper in the "red spots". Jones and Parr (166) reported iron or copper indispensable to the salt oxidation, since salt, iron, nor copper alone damaged the silk; they found that copper increased the reaction so rapidly that silk was tendered while still at the mill. Lloyd (181) has described silk itself as an oxygen carrier and has suggested that any chromium salt present might also act as an oxygen carrier.

Recent studies by Damon (66) tend to show that sodium chloride is the destructive agent of sweat, although Southard (261) found that decrease in breaking strength of two weighted silk fabrics was affected more by variation in the pH of sweat than by variation in its sodium chloride content. Southard's data are shown in Table 14.

Table 14

Effect of Sweat on Breaking Strength of Silk

Breaking strength: warp (pounds per inch)	filling (pounds per inch)	Sweat: pH when fresh	pH when used	sodium chloride (per cent)	Ageing: time (days)	temperature (°C.)
Piqué						
74.3	32.2	---	---	----	Untreated	
68.4	30.6	---	---	0	Water	
68.6	27.6	7.02	7.02	0.2936	0	---
70.6	30.6	7.02	7.02	0.2936	15	35
64.9	31.8	7.02	7.02	0.2936	15	0
67.3+	31.3+	6.47	6.51	0.1949	15	35
70.2+	35.7+	6.47	7.27	0.1941	15	0
71.3+	28.6+	---	---	----	Untreated	
Crêpe						
67.1	19.9	---	---	----	Untreated	
67.1	23.7	---	---	----	Water	
63.1	20.2	6.39	6.78	0.1860	0	---
		5.74	5.74	0.3721	0	---
57.4	19.2	6.78	6.78	0.1965	15	35
64.5	19.2	6.78	5.65	0.1965	15	0
46.2+	17.6+	6.39	6.62	0.1860	15	35
49.5+	19.6+	6.39	7.50	0.1860	15	0
50.9+	16.8+	---	---	----	Untreated	

+Samples sterilized before treating with sweat.

Ageing with sweat caused a decrease in breaking strength of the fabrics studied, and this decrease was greater the higher the temperature. The change of pH values on standing is in agreement with the results of Scott (233), who observed that sweat lost its acidic character and gradually became quite alkaline.

Roberts and Mack (220) have treated silk and weighted silk with artificial acid and alkaline sweat, and have reported that

previous exposure to air and indoor daylight considerably affected the results.

Degradation of Silk by Steam

Silk may come in contact with steam during the course of its fabrication, that is, in certain degumming processes, dyeing, conditioning, and twist setting, and in maintenance where it may be subjected to steam sterilization and pressing.

Early methods for purification of silk fibroin involved the use of steam as described in Table 15:

Table 15

The Preparation of Fibroin

Investigator	Year	Temperature of steam °C.	Pressure of steam atmosphere	Time hour
Anonymous (22)	1836	---	3 - 4	1.5
Cramer (65)	1865	100	1	24
		133	3	3, twice
Fischer and Skita (94)	1901	117 - 120	-	3, twice or three times
Pfannl (211)	1910	130	-	5, twice

It was observed that such degumming lowered the elasticity (65), luster, and softness of the silk (94). Thompson (272) reported that 9.5 per cent of silk dissolved upon boiling in water for three hours; Fischer and Skita (94) found that 70 per cent of silk dissolved upon boiling in water for 300 hours; and Bolley and Schoch (44) found Yama-mai silk lost 13.6 per cent in weight when boiled in water for 24 hours.

Steam has been used in commercial degumming (225) together with small amounts of weak alkali (33, 89, 219), with ordinary soap degumming (23, 153, 269), or with weak acids (50). Takamine (268) recommended the use of 50 pounds of steam for fifteen minutes, followed by steaming for 15 minutes in the presence of weak alkali. Water baths under pressure have been recommended for removing ionizable impurities from silk which is to be used for electrical insulation (180). Recent work (206) has shown that degumming is complete in 10 hours at 100°C., or in three hours at 120°, 130°, or 150°C., although such treatment results in a breakdown of the submicroscopic structure of the fiber.

Steam at 130°C. has been recommended for the separation of wool from wool-silk unions (173), the silk being comparatively stable while the wool may be rubbed to a powder.

After it was learned that bleached silk absorbs 36.5 per cent of moisture from an atmosphere saturated with steam at 100°C. (228), steam was employed as a conditioning agent for yarn (270) and as a means of effecting the setting of pile (160) and twist (55).

One of the older methods of obtaining crêpe effects in fabric was to subject silk or silk unions to a short treatment of five to ten minutes with steam at four to five atmospheres (101).

Elliot has compared the effect on silk of the moist heat of an autoclave and the dry heat of an oven (82) as shown in

Table 16.

Table 16

The Effect of Heat on the Breaking Strength of a Silk Fabric

Time: 25 hours

Heat	Temperature °C.	Loss in breaking strength dry per cent	wet per cent
Dry	100	12	26
	120	38	64
Moist	100	58	40
	120	74	94

A rather short treatment with steam, known as ageing, is often used to develop certain types of dyes. For azo dyes applied in the reduced condition, Adams (15) has recommended ageing for one to six minutes at 212° to 220°F., using dry or wet steam. Durand and Huguenin (77) have recommended one hour of light steam pressure for certain chrome dyeings on silk and eight minutes for mordant dyes (79), while Metzl (195) has recommended not over ten-minute periods of steaming for certain acid and substantive dyes. Hydrosulfite reserves on vat-dyed silk have also been steamed (78). Kaufmann (171) has stated that ageing is not especially hazardous, but that too strenuous steaming weakens silk.

A method for bleaching wild silk involves steaming under pressure for two hours after impregnating the silk with concentrated hydrogen peroxide (238).

Fort has observed that steaming causes a browning of silk

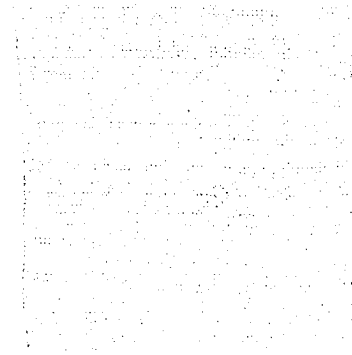
(97), and Johnson (161) has found that silk cannot be heated above 100°C. without injury if moisture is present.

Steam has seldom been recommended for the sterilization of silk, as it has been used for cotton and sometimes for wool, although it is occasionally sterilized in this manner in union textiles. Fulton and Staniford (99) have found that wool may be safely sterilized by twelve pounds of steam in ten minutes, or at atmospheric pressure in one hour, provided a vacuum be established before introduction of the steam. Packaged textile fabrics are sometimes sterilized by steam (283), and the use of steam at 60 to 75 pounds has been recommended to the drycleaning trade for the steam pressing of garments (46, 103) with the caution that if moisture is present the silk may shrink.

EXPERIMENTAL PROCEDURE

Materials

The fibroin used for these studies consisted of plain-woven mulberry silk fabric which was purchased in the gum, and a plain-woven wild silk fabric, pongee. Silk Fabric I was used in all the hydrolyses of silk fibroin, Fabric II in the oxidation and reduction of silk fibroin, and Fabric III in all tests involving wild silk fibroin.



Fabric I Fabric II Fabric III

The chemicals used include:

1. Acetic acid. C. P. Grasselli.
2. Boric acid. U. S. P. Mallinckrodt Chemical Works.
3. Copper sulfate. C. P. General Chemical Co.
4. Ether. Anhydrous, sp. gr. 0.72. General Chemical Co.
5. Hydrochloric acid. C. P., sp. gr. 1.18 - 1.19. General Chemical Co.
6. Hydrogen peroxide. 30 per cent solution. General Chemical Co.
7. Indigo. Synthetic. National Aniline and Chemical Co.
8. Mercury. C. P. Mallinckrodt Chemical Works.
9. Potassium iodide. Reagent. General Chemical Co.
10. Potassium permanganate. C. P. General Chemical Co.
11. Potassium sulfate. Reagent. General Chemical Co.
12. Potassium sulfide. Fused lump. General Chemical Co.
13. Soap. Olate soap flakes. Procter and Gamble Co.
14. Sodium bisulfite. C. P. General Chemical Co.
15. Sodium chloride. C. P. General Chemical Co.

16. Sodium hydrosulfite. Practical. Eastman Kodak Co.

17. Sodium hydroxide. C. P. General Chemical Co.

18. Sodium oxalate. Reagent. Merck.

19. Sodium thiosulfate. Reagent. General Chemical Co.

20. Sulfuric acid. C. P., sp. gr. 1.84. General Chemical Co.

21. Zinc. Mossy. Wilkens-Anderson Co.

Preparation of Fibroin

The raw silk fabric was degummed by boiling for one hour in one hundred volumes of ten per cent neutral soap solution. After rinsing in distilled water, the process was repeated. The silk was rinsed and then boiled for fifteen minutes in distilled water; this process was repeated three times with intermediate rinsings.

The wild silk fabric was boiled for one hour in one hundred volumes of distilled water and rinsed in cold distilled water until the washings were no longer turbid. The fabric was boiled in distilled water for fifteen minutes and again thoroughly rinsed.

The prepared fibroins yielded the following analysis:

Fibroin	Nitrogen per cent	Ash per cent
Silk fibroin I	18.69	0.23
Silk fibroin II	18.58	0.34
Wild silk fibroin III	18.24	0.60

Samples weighing approximately four grams were prepared by cutting pieces of 156 square inches from Fabric I, 100

square inches from Fabric II, and 217 square inches from Fabric III. Yarns were ravelled from the edges so as to avoid loss of yarns during subsequent treatment.

Samples of Fabrics I and II for breaking strength tests were cut 1 3/16 inches wide and 7 inches long, with the length parallel to the warp yarns; those of Fabric III were cut 1 1/4 inches wide and 7 inches long. Yarns were ravelled from the sides of these strips until the width was exactly one inch.

All samples were extracted continuously for 18 hours with anhydrous ether in a modified Soxhlet apparatus to remove fatty and waxy impurities. All four-gram samples were dried to constant weight ($\pm$ 0.0004 g. by the method of tares) at 105°C.

General Procedure

Weighed samples of silk fibroin were treated at 25°C. and at 40°C. by immersion for ten hours in measured portions of test solutions placed in tightly stoppered 250-cc. test tubes or 500-cc. Erlenmeyer flasks which were maintained at constant temperature, $\pm$ 0.1°C., in a De Khotinsky thermostat. The test solutions were brought to constant temperature in the water bath thirty minutes before entering the samples.

For the tests carried out at boiling temperature, the samples were placed in 250-cc. portions of test solutions contained in 500-cc. balloon flasks fitted with reflux condensers and heated over a boiling water bath. Titration of blank solutions showed no concentration of the test solutions during

boiling.

At least five weighed samples and ten breaking strength samples were used for each test, each set of ten breaking strength samples being treated with the same volume of reagent as each four-gram sample.

Blank determinations were made with the silk using zero concentration of the reagent being studied. The weight, nitrogen, breaking strength, and elongation of the residual fibroin in each series of tests are referred to these determinations as 100 per cent.

After the period of treatment, all samples were at once washed free from the test solution. The large samples were air-dried before being brought again to constant weight at 105°C., and analyzed. The strips were broken wet immediately after washing.

Preparation and Analysis of Test Solutions

1. Hydrogen peroxide

Solutions of hydrogen peroxide were made by dilution of thirty per cent reagent with distilled water. These solutions were made 0.01 N with respect to sodium carbonate by addition of 1.86 cc. of 1.0850 N sodium carbonate to each 200-cc. portion of reagent just before entering the samples. A blank solution was titrated at once by Weber's method (286): 2 cc. of the solution were pipetted into 50 cc. of distilled water, 50 cc. of dilute (1:10) sulfuric acid were added,

and the solution was titrated at once to a faint pink coloration with approximately tenth normal potassium permanganate.

2. Hypochlorous acid.

Sodium hypochlorite was prepared by warming 100 g. of bleaching powder with one liter of distilled water, and adding 65 g. of sodium carbonate dissolved in water. The mixture was diluted to two liters and allowed to settle before filtration. This solution was diluted to the desired concentration, and standardized by addition from a burette to 25 cc. of 10 per cent potassium iodide which had been acidified with hydrochloric acid and diluted to 500 cc. The iodine liberated was titrated with standard sodium thiosulfate, using starch paste as an indicator. Just before use, two equivalents of boric acid were added to liberate hypochlorous acid.

3. Potassium permanganate.

Potassium permanganate was dissolved in boiled distilled water and allowed to stand for several days in a tightly stoppered brown glass bottle. The precipitated manganese dioxide was removed by filtration through acid-digested asbestos; the suction flask and stock bottle were well washed with this filtered permanganate solution. The solution was standardized against sodium oxalate in hot sulfuric acid solution (88).

4. Sodium hydrosulfite.

The suspended solids were removed from a twenty per cent solution of sodium hydrosulfite by gentle suction through four layers of filter paper. The filtered solution was made 0.5 N with respect to acetic acid by addition of the calculated amount of standard acid just before use. The acidified solution was standardized at once by the Indigo method of Scott : twenty-five cc. of the sodium hydrosulfite solution were diluted to one liter in a volumetric flask, and the resulting solution was used to titrate 25 cc. of standard Indigo solution in an atmosphere of carbon dioxide.

The Indigo solution was prepared (234) by slowly dissolving 4.2 g. of Indigo in 150 cc. of concentrated sulfuric acid. This solution was digested on a hot plate for one hour at 80° C., cooled, and made up to four liters with distilled water. It was standardized by pipetting 25 cc. into a large porcelain casserole and titrating to an orange-yellow color with approximately hundredth normal potassium permanganate.

5. Hydrochloric acid.

A standard fifth normal hydrochloric acid solution for reference was made by dissolving C. P. hydrochloric acid in chloride-free distilled water and tightly closed to avoid contamination. The solution was standardized gravimetric-

ally by conversion into silver chloride. The normality was checked several times during the course of this work. All alkali, acid, and sodium chloride concentrations refer to this standard.

The hydrochloric acid solutions used for hydrolysis of fibroin were made by diluting C. P. reagent with distilled water and were standardized with standard fifth normal sodium hydroxide solution in the presence of Methyl Red.

The concentrated hydrochloric acid solution was made by diluting C. P. acid with distilled water to a specific gravity of 1.145, determined at 15°C. by means of a Westphal balance.

6. Sodium hydroxide

The dilute solutions were made by dissolving sodium hydroxide in distilled water to form a saturated solution from which the carbonates precipitated. The solutions were decanted rapidly into water boiled free from carbon dioxide and were kept in stoppered bottles. The alkali was standardized by titration of measured volumes of the standard acid in the presence of Methyl Red.

Concentrated sodium hydroxide solution was prepared by filtering the precipitated carbonates from a saturated solution in boiled distilled water as rapidly as possible, and diluting to sp. gr. 1.410 at 15°C. with cold distilled water boiled free from carbon dioxide.

7. Sodium chloride

The calculated amount of C. P. reagent was dissolved in chloride-free distilled water and the chloride ion was determined volumetrically by the Mohr method (88), by titration in neutral solution with fifth normal silver nitrate using potassium chromate as an indicator.

The silver nitrate was standardized by titrating a measured volume of standard hydrochloric acid solution made neutral to Methyl Red by the addition of dilute chloride-free ammonium hydroxide. The titration was carried out in a porcelain casserole using potassium chromate as the indicator.

Analytical Methods for Silk

1. Physical testing of fabric

The wet breaking strength of the silk fabrics was determined by the one-inch strip method (274), with a Scott Universal Tester and Autographic Recorder. The two-inch jaws of the machine were clamped three inches apart in the fabric, and the machine was run at the rate of twelve inches per minute until the fabric was strained to the breaking point. Breaking strength was recorded in pounds, and elongation of fabric at the breaking load was determined from the stress-strain curves drawn by the Recorder.

2. Loss in weight

The large samples of fibroin were brought to constant weight by heating at 105°C., both before and after treatment.

3. Kjeldahl method

A modified Kjeldahl method was used for determination of total nitrogen. Weighed samples of fibroin (about 4 g.) were digested in 500-cc. Kjeldahl flasks with 50 cc. of concentrated sulfuric acid, 10 g. of potassium sulfate, 1 g. of copper sulfate, and one drop of mercury. The digestion was continued until the reaction mixture became clear light blue. After the flasks were cooled, 200 cc. of distilled water were added to each. In order to distil the ammonia, 30 cc. of 10 per cent potassium sulfide and 160 cc. of 40 per cent sodium hydroxide, a small piece of paraffin, and several small pieces of mossy zinc were added to each flask. The ammonia was distilled at once through water-cooled condensers of block tin into an excess of standard acid. The excess acid was titrated with standard sodium hydroxide, using Methyl Red as indicator. Blank determinations were made with the reagents.

Oxidation of Fibroin

Silk fibroin and wild silk fibroin were oxidized for ten hours at 40°C. by alkaline hydrogen peroxide. Solutions 2.1800 N and 4.3601 N were used in order to determine the effect of increasing concentration of oxidizing agent. After treatment in 200-cc. portions of peroxide, made 0.01 N as to sodium carbonate, the silk was washed in distilled water until the washings no longer decolorized dilute potassium permanganate

solution acidified with sulfuric acid. Tables 17 and 18 show the changes in weight, nitrogen, wet warp breaking strength and elongation at the breaking load of silk fibroin and wild silk fibroin brought about by aqueous hydrogen peroxide. Figure I illustrates these data in graphical form.

A second type of oxidizing agent employed in textile technology, hypochlorous acid, was used in the concentration 0.2350 N at 40°C. for ten hours, to oxidize both silk and wild silk fibroin. After treatment, the fabric was washed in distilled water until the washings no longer gave an opalescence with silver nitrate; the samples were air-dried and analyzed for nitrogen without drying to constant weight at 105°C. Table 19 shows the effect of hypochlorous acid upon the two fibroins.

A third type of oxidizing agent, potassium permanganate, was used in two series of tests. Samples of both silk and wild silk fibroin were oxidized for ten hours at 40°C. by 200-cc. portions of 0.1973 N potassium permanganate in neutral solution. After oxidation, the fibroin was freed from manganese dioxide by working it in several fresh, 200-cc. portions of 0.5 per cent sodium bisulfite solution for one hour, and then washing it in distilled water until the washings no longer decolorized potassium permanganate. Table 20 shows the effect of potassium permanganate upon silk and wild silk fibroin.

A second series of tests was carried out at 40°C. for ten hours, varying the volume of the 0.1973 N permanganate bath

from 200 cc. to one liter. The manganese dioxide was dissolved by working the samples for two hours in 0.5 per cent sodium bisulfite. Table 21 shows the effect of increasing volume of 0.1973 N potassium permanganate upon wild silk fibroin. Figure II shows the values for nitrogen and weight of the residual fibroin plotted as functions of the grams of potassium permanganate per gram of silk.

Table 17

Effect of Hydrogen Peroxide on Silk Fibroin

Time: 10 hours
Temperature: 40°C.
Sodium carbonate: 0.01 N

Determination	Hydrogen peroxide	Silk	Residue					
			Weight		Nitrogen		Breaking strength of wet warp	Elongation at breaking load
number	normality	gram	gram	per cent	gram	per cent	pound per inch	per cent
1	0	3.9835	3.9747	99.8	0.7441	18.68		
2		4.0906	4.0805	99.7	0.7596	18.57		
3		4.0663	4.0550	99.7	0.7574	18.63		
4		4.1187	4.1128	99.9	0.7631	18.53		
5		4.5216	4.5164	99.9	0.8423	18.63		
Average				99.8		18.61	26	25
1	2.1800	4.3243	4.2175	97.5	0.7855	18.16		
2		4.3514	4.1982	96.5	0.7815	17.96		
3		4.2883	4.1497	96.8	0.7746	18.06		
Average				96.9		18.06	17	15
1	4.3601	4.2006	3.8649	92.0	0.7175	17.08		
2		4.5733	4.1929	91.7	0.7812	17.08		
3		4.1080	3.9513	96.2	0.7038	17.13		
Average				93.3		17.10	<1	

Table 18

Effect of Hydrogen Peroxide on Wild Silk Fibroin

Time: 10 hours
Temperature: 40°C.
Sodium carbonate: 0.01 N

Determination number	Hydrogen peroxide normality	Silk	Residue					
			Weight		Nitrogen		Breaking strength of wet warp pound per inch	Elongation at breaking load per cent
		gram	gram	per cent	gram	per cent		
1	0	4.3954	4.3506	99.0	0.7957	18.10		
2		4.8402	4.7918	99.0	0.8813	18.21		
3		4.2524	4.2119	99.0	0.7724	18.16		
Average				99.0		18.16	16	25
1	2.1800	4.4146	4.3020	97.4	0.7920	17.94		
2		4.3324	4.2268	97.6	0.7792	17.99		
3		4.4399	4.3366	97.7	0.7963	17.94		
4		4.6494	4.5399	97.6	0.8337	17.93		
Average				97.6		17.95	12	17
1	4.3601	4.1763	4.0311	96.5	0.7372	17.65		
2		3.9516	3.7943	96.0	0.6970	17.64		
3		3.9996	3.8586	96.5	0.7078	17.70		
4		4.0071	3.8524	96.1	0.7050	17.59		
Average				96.3		17.65	11	16

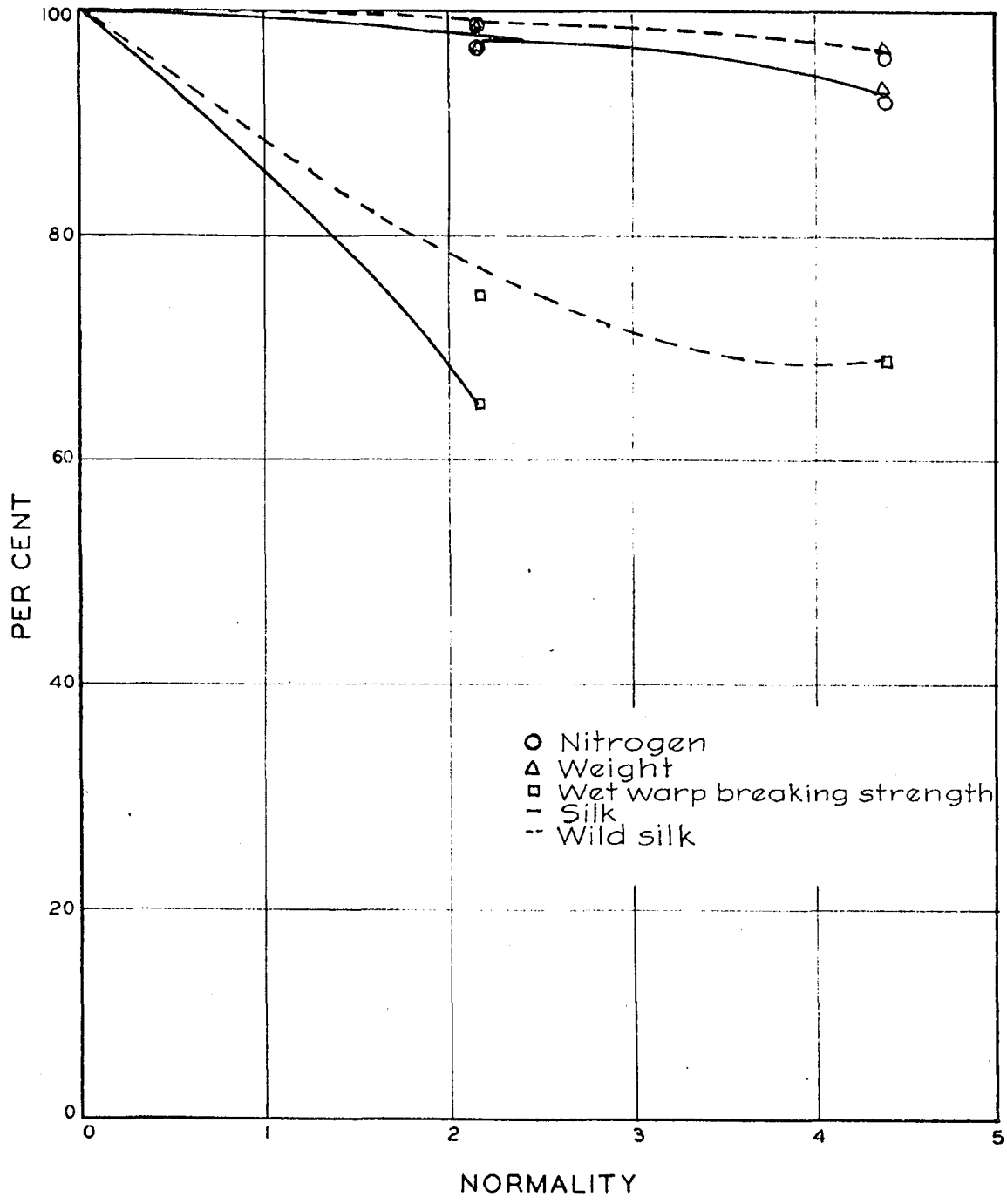


Figure I. Effect of hydrogen peroxide in ten hours at 40°C. on the weight, nitrogen, and wet warp breaking strength of silk and wild silk fibroin. Solutions 0.01 N as to sodium carbonate.

Table 19

Effect of Hypochlorous Acid on Silk Fibroin and Wild Silk Fibroin

Time: 10 hours
Temperature: 40°C.

Determination number	Fibroin	Hypochlorous acid normality	Silk	Residue			
				Nitrogen		Breaking strength of wet warp	Elongation at breaking load
			gram	gram	per cent	pound per inch	per cent
1	Silk	0	4.1531	0.7720	18.59		
2			4.3654	0.8116	18.59		
3			4.4263	0.8217	18.56		
4			4.1454	0.7704	18.58		
Average					18.58	31	27
1		0.2350	3.9268	0.6664	16.97		
2			4.0005	0.6847	17.12		
3			3.8399	0.6557	17.08		
Average					17.06	< 1	
1	Wild silk	0	4.3448	0.7950	18.30		
2			4.2063	0.7673	18.24		
3			4.0712	0.7400	18.18		
Average					18.24	16	25
1		0.2350	4.1972	0.7131	16.99		
2			3.8055	0.6427	16.89		
3			3.9965	0.6711	16.79		
Average					16.89	< 1	

Table 20

Effect of Potassium Permanganate on Silk Fibroin and Wild Silk Fibroin

Time: 10 hours
Temperature: 40°C.
Volume of reagent: 200 cc.

Determination number	Fibroin	Potassium permanganate normality	Silk Weight gram	Residue Weight gram	Residue Weight per cent	Residue Nitrogen gram	Residue Nitrogen per cent	Breaking strength of wet warp pound per inch	Elongation at breaking load per cent
1	Silk	0	4.2520	4.2349	99.6	0.7903	18.59		
2			4.2860	4.2582	99.3	0.7978	18.61		
3			4.0370	4.0078	99.3	0.7483	18.54		
4			4.2557	4.2247	99.3	0.7879	18.51		
Average					99.4		18.56	27	26
1		0.1973	4.1380	4.0224	97.2	0.7455	18.02		
2			4.6374	4.5325	97.7	0.8369	18.05		
3			4.6446	4.5479	97.9	0.8453	18.20		
Average					97.6		18.09	<1	
1	Wild silk	0	4.3795	4.3569	99.5	0.7892	18.25		
2			4.6515	4.6315	99.6	0.8519	18.31		
3			3.9894	3.9703	99.5	0.7250	18.17		
4			4.3526	4.3285	99.4	0.7943	18.25		
Average					99.5		18.24	16	26

Table 20, Cont'd.

1	0.1973	4.4606	4.3000	96.4	0.7965	17.86	
2		3.6338	3.4901	96.0	0.6453	17.76	
3		4.0640	3.9202	96.5	0.7222	17.70	
4		4.2191	4.0776	96.6	0.7531	17.85	
Average				96.4		17.79	<1

Table 21

Effect of Volume of 0.1973 N Potassium Permanganate on Wild Silk

Time: 10 hours
Temperature: 40°C.

Determination number	Volume of reagent cc.	Potassium permanganate gram per gram of silk	Silk gram	Residue Weight gram	Residue Weight per cent	Residue Nitrogen gram	Residue Nitrogen per cent
1	200 cc. water,		3.9894	3.9703	99.5	0.7250	18.17
2	followed		4.3795	4.3569	99.5	0.7992	18.25
3	by bisulfite		4.6515	4.6315	99.6	0.8519	18.31
4			4.3526	4.3285	99.4	0.7943	18.25
Average					99.5		18.24
1	200	0.4660	4.4606	4.3000	96.4	0.7965	17.86
2		0.5720	3.6338	3.4901	96.0	0.6453	17.76
3		0.5115	4.0640	3.9202	96.5	0.7222	17.70
4		0.4927	4.2191	4.0776	96.6	0.7531	17.85
Average					96.4		17.79
1	500	1.4472	3.5906	3.3273	92.7	0.6110	17.02
2		1.3434	3.8681	3.6377	94.0	0.6627	17.13
Average					93.4		17.08
1	1000	2.3581	4.4072	3.6949	83.8	0.6933	15.73
2		2.4007	4.3290	3.5916	83.0	0.6717	15.51
Average					83.4		15.62

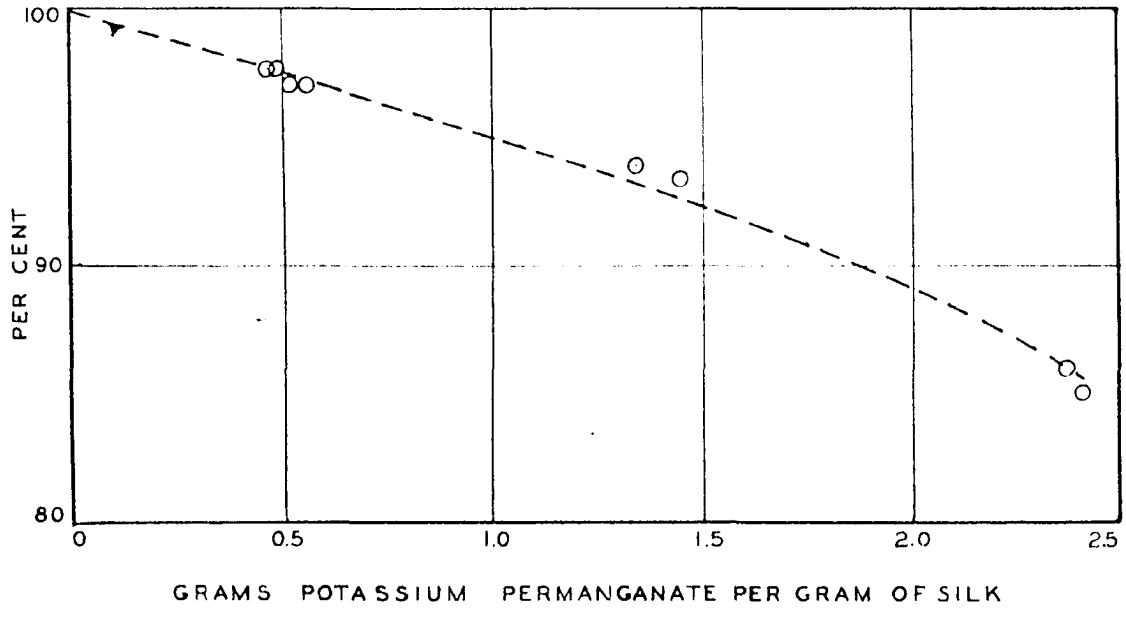


Figure II a. Effect of different amounts of 0.1973 N potassium permanganate in ten hours at 40°C. on the nitrogen of wild silk fibroin.

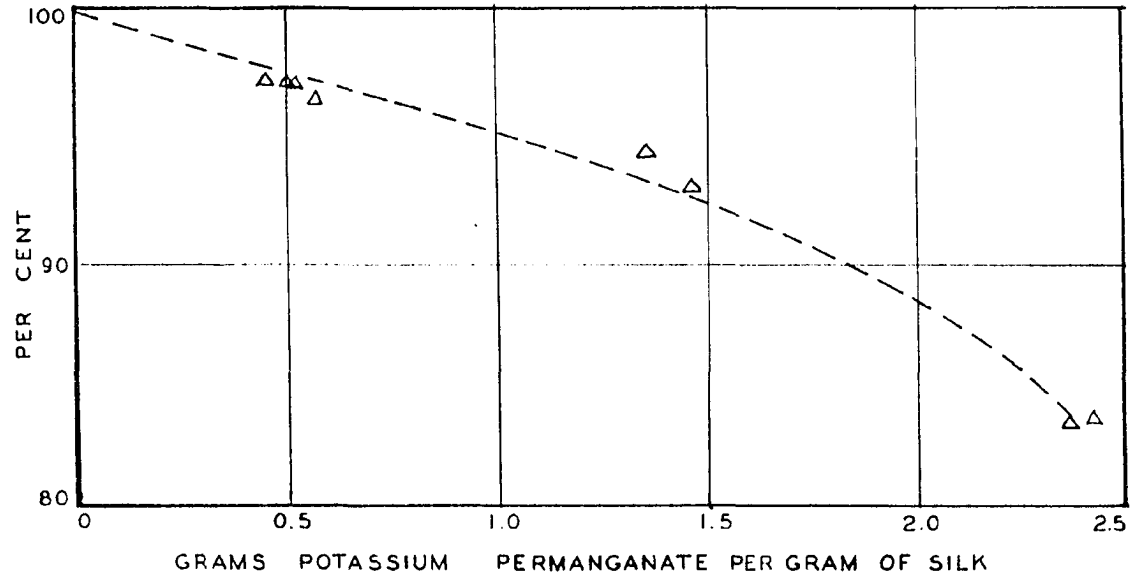


Figure II b. Effect of different amounts of 0.1973 N potassium permanganate in ten hours at 40°C. on the weight of wild silk fibroin.

Oxidizing agents have been shown to effect considerable degradation of silk, the amount increasing with increasing concentration. Wild silk has been shown more stable than silk to the action of three oxidizing agents, hydrogen peroxide, hypochlorous acid, and potassium permanganate, in agreement with observations recorded in the literature.

Potassium permanganate and hydrogen peroxide bleached silk equally well, leaving it slightly yellowed, or over-bleached. Wild silk was bleached almost white by permanganate, and a light brownish-yellow by peroxide. Hypochlorous acid did not bleach the silks but caused a distinct browning of both fabrics; qualitative tests showed the presence of chlorine in these fibroins.

Two factors in the greater degradation of fibroin by potassium permanganate than by hydrogen peroxide are the dissipation of the oxidizing power of hydrogen peroxide by the evolution of oxygen and the building up of an appreciable concentration of alkali by potassium permanganate in neutral solution. Blank determinations testing 2.1800 N and 4.3601 N hydrogen peroxide decreased to 0.4926 N and 1.5332 N, respectively, within ten hours at 40°C. Since each molecular portion of potassium permanganate liberates a molecular portion of potassium hydroxide according to the equation,

$$2\ KMnO_4 + H_2O \longrightarrow 2\ KOH + 2\ MnO_2 + 3(O),$$

0.1973 N potassium permanganate in neutral solution becomes

0.0658 N with respect to potassium hydroxide upon complete decomposition of the permanganate.

Oxidative degradation of silk by potassium permanganate in neutral solution has been shown to be a linear function of the volume of reagent used. This fact is in accord with the known behavior of manganese dioxide as a catalyst for the further decomposition of potassium permanganate.

The mechanical failure of both silk and wild silk brought about by oxidative degradation has been shown to be more rapid than loss in weight or nitrogen, indicating a breakdown of fibrous structure preceding the formation of soluble decomposition products.

Reduction of Fibroin

Wild silk and degummed silk fibroin were immersed separately for 10 hours at 40°C. in 200-cc. portions of 0.1844 N sodium hydrosulfite which had been acidified by addition of 0.5 mols per liter of acetic acid. The treated samples were washed in distilled water until the washings no longer decolorized potassium permanganate. Blank determinations were made in the same way with 0.5 N acetic acid. Table 22 shows the effect of sodium hydrosulfite upon weight, nitrogen, wet warp breaking strength, and elongation at breaking load of the two fabrics.

Table 22

Effect of Sodium Hydrosulfite on Silk Fibroin

Time: 10 hours
Temperature: 40°C.
Acetic acid: 0.5 N

Determination number	Fibroin	Sodium hydrosulfite normality	Silk Weight gram	Residue Weight gram	Residue Weight per cent	Residue Nitrogen gram	Residue Nitrogen per cent	Breaking strength of wet warp pound per inch	Elongation at breaking load per cent
1	Silk	6	4.1942	4.1780	99.6	0.7720	18.41		
2			4.2268	4.2063	99.5	0.7835	18.54		
3			4.2329	4.2082	99.4	0.7839	18.52		
4			4.2714	4.2548	99.6	0.7883	18.46		
Average					99.5		18.48	25	26
1		0.1844	4.3694	4.3601	99.8	0.8078	18.49		
2			4.4216	4.4104	99.7	0.8090	18.30		
3			4.3513	4.3415	99.8	0.7965	18.30		
Average					99.8		18.36	28	25
1	Wild silk	0	4.2491	4.2225	99.4	0.7756	18.25		
2			4.3425	4.3157	99.4	0.7927	18.25		
3			4.3141	4.2855	99.3	0.7898	18.31		
4			4.3861	4.3609	99.4	0.7981	18.20		
Average					99.4		18.25	14	24
1		0.1844	4.5931	4.5832	99.8	0.8341	18.16		
2			4.1701	4.1619	99.8	0.7592	18.21		
3			4.0895	4.0782	99.7	0.7424	18.15		
4			4.6443	4.6442	100.0	0.8472	18.24		
Average					99.8		18.19	14	23

The small differences which have been found between the untreated and the reduced fibroins, in case of both silk and wild silk, come within the limits of experimental error. These quantitative data confirm the observations reported in the trade literature.

Acid Degradation of Fibroin

Wild silk fibroin was subjected to hydrolysis for ten hours at 40°C. by 0.4977 N, 1.0263 N, 1.2264 N, and 2.1216 N hydrochloric acid, and to hydrolysis for one hour at 100°C. by 0.0304 N, 0.1019 N, and 0.1950 N hydrochloric acid. After hydrolysis, the silk was washed in distilled water until the wash water no longer showed opalescence with silver nitrate. Tables 23 and 24 summarize the results of these hydrolyses. Figures III and IV compare the acid degradation of silk and wild silk.

Silk fibroin, as well as wild silk fibroin, was treated with concentrated hydrochloric acid under conditions similar to those recommended for the production of special finishes. Samples were wet with distilled water, centrifuged for one minute, and then immersed in 100-cc. portions of hydrochloric acid, sp. gr. 1.145, contained in 600-cc. beakers and brought to 15°C., ± 0.1°, in a thermostat. The silk was stirred gently in the test solution for thirty seconds, as measured by a stop watch, and then vigorously stirred for a few seconds in a

liter of distilled water and washed rapidly in successive portions of distilled water until free from chlorides. Table 25 presents the effect of concentrated acid on fibroin and wild silk fibroin.

Table 23

Effect of Hydrochloric Acid on Wild Silk Fibroin

Time: 10 hours
Temperature: 40°C.

Determination number	Hydrochloric acid normality	Silk grams	Residue Weight grams	Residue Weight per cent	Residue Nitrogen grams	Residue Nitrogen per cent of silk	Residue Nitrogen per cent of residue	Breaking strength of wet warp pound per inch	Elongation at breaking load per cent
1	0	4.4417	4.4199	99.5	0.8091	18.22	18.31		
2		4.2785	4.2553	99.5	0.7820	18.28	18.38		
3		4.6744	4.6507	99.5	0.8542	18.27	18.37		
4		4.4378	4.4172	99.5	0.8083	18.21	18.30		
Average				99.5		18.25	18.34	16	25
1	0.4977	4.1354	4.0984	99.1	0.7528	18.20	18.37		
2		4.4548	4.4153	99.1	0.8106	18.20	18.36		
Average				99.1		18.20	18.36	15	25
1	1.0263	4.5424	4.4878	98.8	0.8233	18.12	18.34		
2		4.2510	4.1975	98.7	0.7707	18.13	18.36		
3		4.4107	4.3575	98.8	0.7956	18.04	18.31		
		4.4944	4.4388	98.8	0.8118	18.06	18.29		
Average				98.8		18.09	18.32	12	21

Table 23, Cont'd.

1	1.2664	4.4774	4.4157	98.6	0.8076	18.04	18.29		
2		3.7732	3.7142	98.4	0.6833	18.11	18.40		
3		3.9633	5.9019	98.4	0.7169	18.09	18.37		
4		4.4355	4.3705	98.5	0.7999	18.03	18.30		
5		4.6695	4.6065	98.6	0.8450	18.10	18.34		
Average				98.5		18.07	18.34	10	19
1	2.1216	4.0273	3.9082	97.0	0.7137	17.72	18.25		
2		4.1003	3.9861	97.2	0.7239	17.66	18.16		
3		4.6111	4.4834	97.2	0.8059	17.48	17.97		
Average				97.1		17.62	18.13	5	8

Table 24

Effect of Hydrochloric Acid on Wild Silk Fibroin

Time: 1 hour
Temperature: 100°C.

Determination number	Hydrochloric acid normality	Silk	Residue						
			Weight			Nitrogen			
		gram	gram	per cent	gram	per cent of silk	per cent of residue	Breaking strength of wet warp pound per inch	Elongation at breaking load per cent
1	0	4.3277	4.2941	99.2	0.7798	18.02	18.16		
2		4.5014	4.4690	99.3	0.8112	18.02	18.15		
3		4.4223	4.3944	99.4	0.7978	18.04	18.16		
Average				99.3		18.03	18.16	17	27
1	0.0304	4.3568	4.2977	98.6	0.7906	18.15	18.40		
2		4.4630	4.3974	98.5	0.8023	17.99	18.26		
Average				98.6		18.07	18.33	13	17
1	0.1019	4.7541	4.5398	95.5	0.8436	17.74	18.58		
2		4.2256	4.1170	97.5	0.7518	17.80	18.26		
Average				96.5		17.77	18.42	7	14
1	0.1950	4.3135	4.1572	95.9	0.7646	17.73	18.48		
2		4.2546	4.0759	95.8	0.7517	17.67	18.44		
3		4.4307	4.2599	96.1	0.7653	17.69	18.40		
Average				95.9		17.70	18.44	5	7

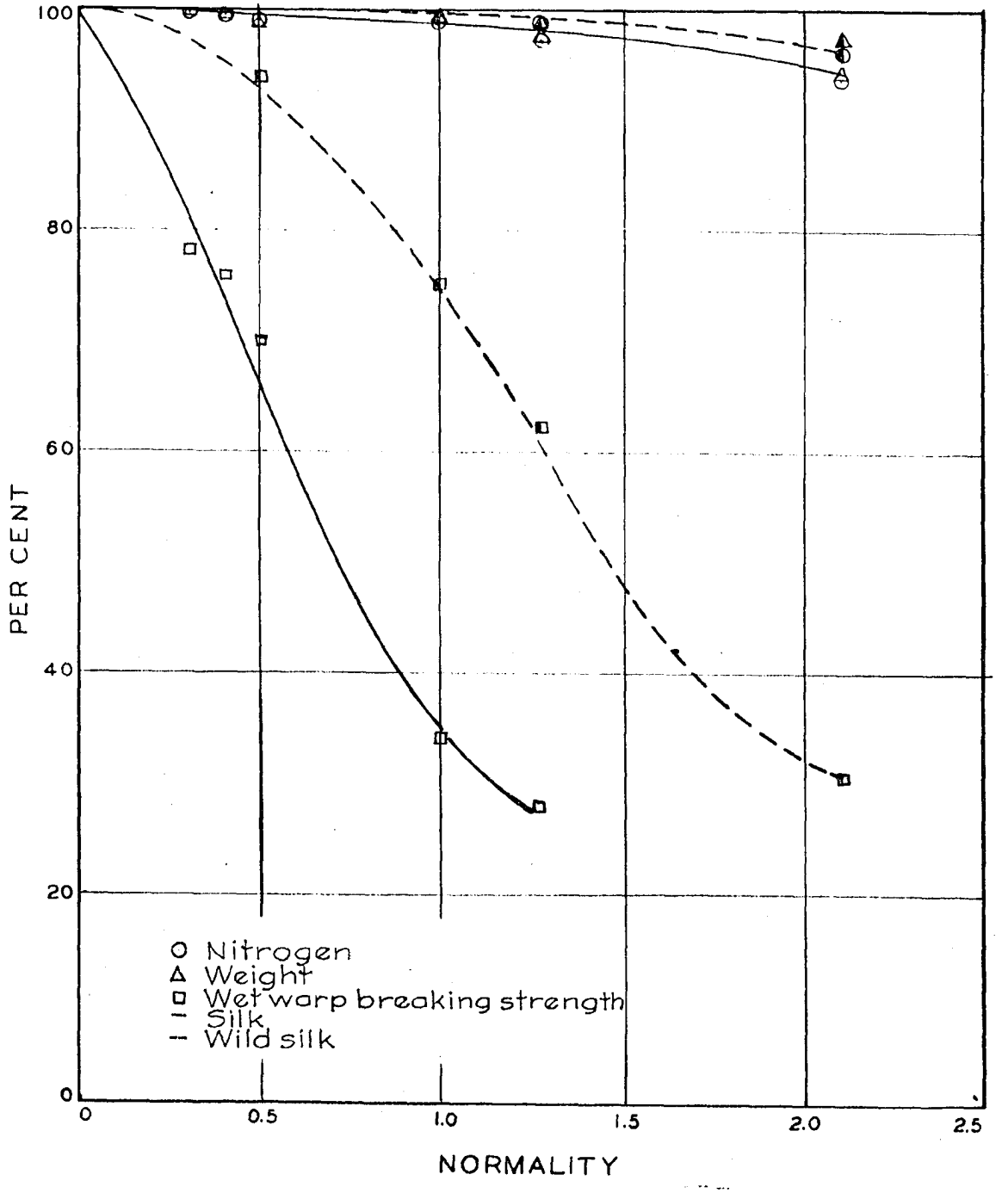


Figure III. Effect of hydrochloric acid in ten hours at 40°C. on the weight, nitrogen, and wet warp breaking strength of silk and wild silk fibroin.

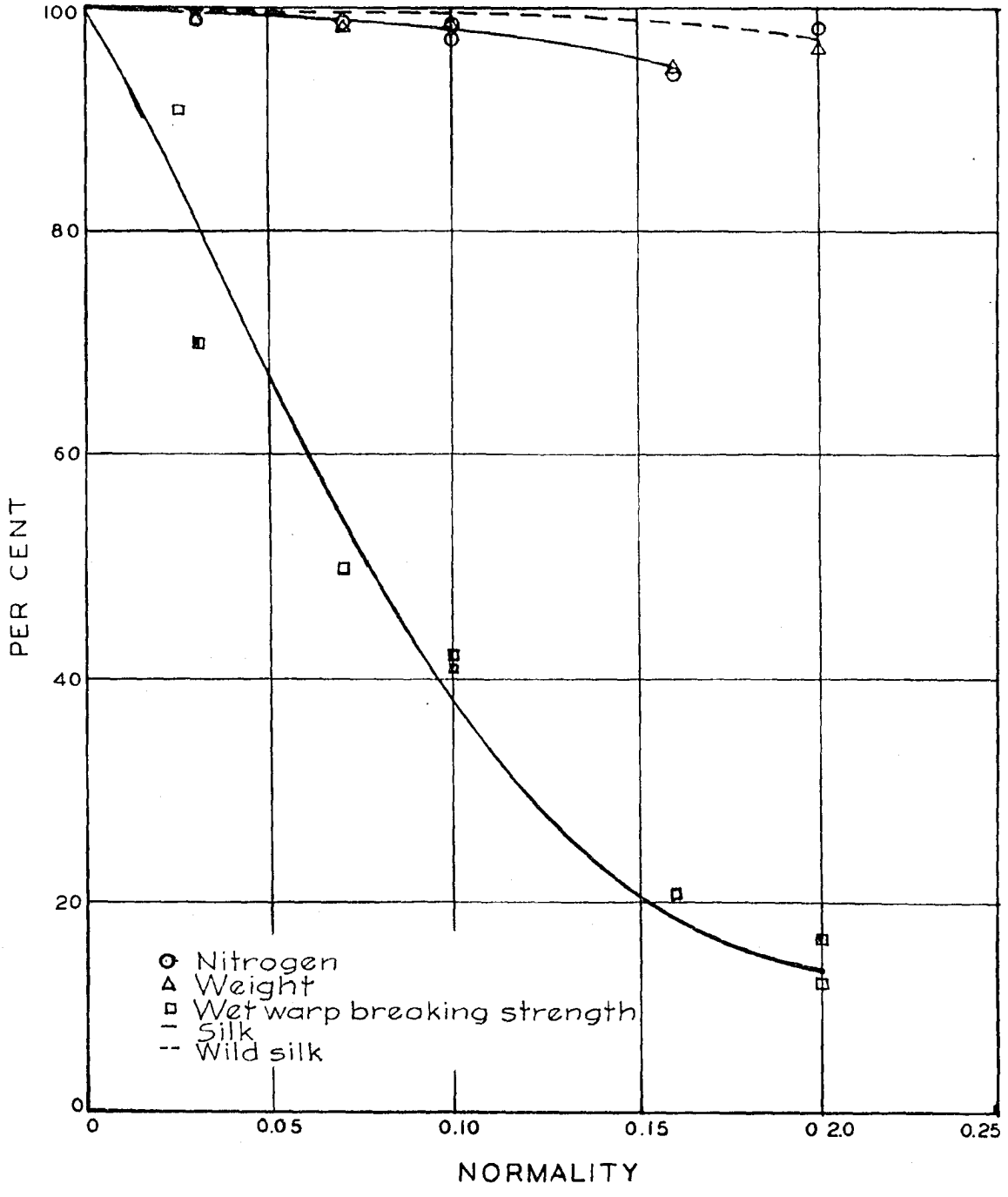


Figure IV. Effect of hydrochloric acid in one hour at 100°C. on the weight, nitrogen, and wet warp breaking strength of silk and wild silk fibroin.

Table 25

Effect of Concentrated Acid on Fibroin

Time: 0.5 minute
Temperature: 15°C.
Hydrochloric acid: 1.145 sp. gr.

Determination number	Fibroin	Treatment	Silk			Residue				
			Weight			Nitrogen			Breaking strength of wet warp	Elongation at breaking load
			gram	gram	per cent	gram	per cent of silk	per cent of residue	pound per inch	per cent
1	Silk	None	4.0626			0.7611	18.73			
2			4.2519			0.7960	18.72			
3			3.9994			0.7471	18.68			
4			4.1912			0.7817	18.65			
5			3.8814			0.7239	18.65			
6			4.1185			0.7711	18.67			
Average					100		18.69	18.69	44	29
1		Acid	3.9105	3.3113	84.7	0.6219	15.90	18.72		
2			4.1591	3.5965	86.5	0.6709	16.13	18.65		
3			3.9247	3.3552	85.5	0.6289	16.02	18.71		
4			3.7250	2.9466	79.1	0.5910	15.87	20.06		
Average					84.0		15.98	19.04	< 1	
1	Wild silk	None	4.3448			0.7950	18.30			
2			4.2063			0.7673	18.24			
3			4.0712			0.7400	18.18			
Average					100		18.24	18.24	16	23
1		Acid	4.4745	4.4381	99.2	0.8080	18.06	18.21		
2			4.4475	4.4083	99.1	0.8086	18.18	18.34		
3			4.1630	4.1205	99.0	0.7568	18.18	18.36		
Average					99.1		18.14	18.30	16	25

Degradation of wild silk by dilute hydrochloric acid has been shown to increase with increasing concentration of acid, the weight and nitrogen of the residual fibroin being logarithmic functions, $y = ax^b$, of the concentration of acid. Acid hydrolysis tends to leave a residue richer in nitrogen than the original fibroin, as does mulberry silk fibroin (280). Weight and nitrogen have been shown to decrease similarly, indicating but little selective solution of portions having different contents of nitrogen. Breaking strength and elongation have been shown to decrease more rapidly than weight and nitrogen.

Wild silk has been quantitatively shown more stable than silk to both dilute and concentrated acid, supporting observations recorded in the literature.

Increase in temperature has been shown to increase the degradation of both silk and wild silk fibroin. This effect of temperature is an important factor to consider in the use of acids in hot dyebaths, since very dilute acid weakens silk perceptibly at 100°C. in one hour.

Concentrated hydrochloric acid, sp. gr. 1.145, was found to cause much shrinkage and gelatinization of silk fibroin and to be impossible for use in producing crêpe effects under the conditions recommended by Depouilly (71, 72) (hydrochloric acid, sp. gr. 1.130 to 1.145, at 5° to 35°C. for one to fifteen minutes) because at 15°C. the silk almost dissolved

in five minutes and was too slimy to handle after one minute. The residual fibroin after one minute amounted to but 71 per cent of its original weight and contained only 13 per cent of nitrogen. However, when a second sample of silk was treated in the same bath, as would be the case in commercial practice, the hydrolysate from the first silk apparently acted as a protective agent toward the second, for the residual fibroin after half a minute in the previously used bath was 94 per cent of its original weight and contained 17 per cent of nitrogen.

Alkaline Degradation of Fibroin

Weighed samples of wild silk fibroin were hydrolyzed for ten hours at 25°C. by 0.3265 N, 0.4169 N, 0.5641 N, and 0.9863 N sodium hydroxide, and for ten hours at 40°C. by 0.2197 N, 0.5641 N, and 0.9863 N sodium hydroxide. At 100°C., 0.0452 N, and 0.0969 N sodium hydroxide were used for one-hour hydrolysis. After treatment, the samples were washed in distilled water until the washings were no longer alkaline to phenolphthalein. The analytical data are shown in Tables 26, 27, and 28, and are illustrated and compared with those for acid degradation by Figures V and VI. Figures VII, VIII, and IX compare the alkaline degradation of silk and wild silk fibroin.

Concentrated alkali, such as that recommended for mercerization and for the production of other special finishes, was used with both silk and wild silk fibroin. Samples, wet and

centrifuged, were placed in 100-cc. portions of sodium hydroxide, sp. gr. 1.410, at 15°C. for five minutes. After treatment, the samples were stirred vigorously into successive liter-portions of distilled water and washed until the rinse was no longer alkaline to phenolphthalein. The results of this treatment with concentrated alkali are shown in Table 29.

Table 26

Effect of Sodium Hydroxide on Wild Silk Fibroin

Time: 10 hours
Temperature: 25°C.

Determination number	Sodium hydroxide normality	Silk	Residue						
			Weight		Nitrogen			Breaking strength of wet warp pound per inch	Elongation at breaking load per cent
		gram	gram	per cent	gram	per cent of silk	per cent of residue		
1	0	4.4105	4.4069	99.9	0.8080	18.32	18.33		
2		4.3656	4.3534	99.8	0.7983	18.29	18.34		
3		4.3023	4.2972	99.9	0.7874	18.30	18.32		
4		4.0834	4.0711	99.7	0.7466	18.28	18.34		
Average				99.8		18.30	18.33	17	26
1	0.2197	4.1879	4.0990	97.9	0.7565	18.06	18.46		
2		4.5365	4.4853	97.8	0.8293	18.08	18.49		
Average				97.9		18.07	18.48	15	26
1	0.4169	4.5880	4.4600	97.2	0.8304	18.10	18.62		
2		4.4368	4.3126	97.2	0.7997	18.02	18.54		
3		4.3816	4.2679	97.4	0.7862	17.94	18.42		
Average				97.3		18.02	18.53	13	22
1	0.5641	4.0945	3.9542	96.6	0.7326	17.89	18.53		
2		4.3024	4.1419	96.3	0.7744	18.00	18.70		
Average				96.5		17.95	18.62	4	7
1	0.9863	4.4670	4.1927	93.9	0.7723	17.29	18.42		
2		4.3578	4.0850	93.7	0.7558	17.34	18.50		
3		4.5871	4.2959	93.6	0.7867	17.15	18.31		
Average				93.7		17.26	18.41	2	5

Table 27

Effect of Sodium Hydroxide on Wild Silk Fibroin

Time: 10 hours
Temperature: 40°C.

Determination number	Sodium hydroxide normality	Silk gram	Residue Weight gram	per cent	Residue Nitrogen gram	per cent of silk	per cent of residue	Breaking strength of wet warp pound per inch	Elongation at breaking load per cent
1	0	4.4417	4.4199	99.5	0.8091	18.22	18.31		
2		4.2785	4.2553	99.5	0.7820	18.28	18.38		
3		4.6744	4.6507	99.5	0.8542	18.27	18.37		
4		4.4378	4.4172	99.5	0.8083	18.21	18.30		
Average				99.5		18.25	18.34	16	25
1	0.2197	4.4057	4.2309	96.0	0.7837	17.79	18.52		
2		4.6459	4.4848	96.5	0.8294	17.85	18.49		
3		4.7409	4.5655	96.3	0.8372	17.67	18.34		
Average				96.3		17.77	18.45	11	19
1	0.5641	4.6665	4.3224	92.6	0.8015	17.18	18.54		
2		4.2751	3.9647	92.7	0.7370	17.24	18.59		
3		4.4538	4.1298	92.7	0.7658	17.19	18.54		
4		4.1290	3.8203	92.5	0.7114	17.23	18.62		
Average				92.6		17.21	18.57	< 1	
1	0.9863	4.1922	3.4560	82.4	0.6379	15.22	18.46		
2		4.2507	3.4772	81.8	0.6478	15.24	18.63		
3		3.9297	3.2400	82.4	0.6011	15.30	18.55		
4		3.9531	3.2507	82.2	0.6005	15.19	18.47		
Average				82.2		15.24	18.53	< 1	

Table 28

Effect of Sodium Hydroxide on Wild Silk Fibroin

Time: 1 hour
Temperature: 100°C.

Determination	Sodium hydroxide	Silk	Residue						
		Weight						Breaking strength of wet warp	Elongation at breaking load
number	normality	gram	gram	per cent	gram	per cent of silk	per cent of residue	pound per inch	per cent
1	0	4.3277	4.3941	99.2	0.7798	18.02	18.16		
2		4.5014	4.4690	99.3	0.8112	18.02	18.15		
3		4.4223	4.3944	99.4	0.7978	18.04	18.16		
Average				99.3		18.03	18.16	17	27
1	0.0452	4.4297	4.2640	96.3	0.7895	17.82	18.52		
2		4.8157	4.6427	96.4	0.8593	17.84	18.51		
3		4.2475	4.0683	95.8	0.7535	17.74	18.52		
4		4.2041	4.0419	96.1	0.7479	17.79	18.50		
Average				96.1		17.80	18.51	8	15
1	0.0969	4.4307	4.1480	93.6	0.7693	17.36	18.55		
2		4.0637	3.8048	93.6	0.7026	17.29	18.47		
3		4.4034	4.1151	93.4	0.7625	17.32	18.54		
4		4.6014	4.2920	93.3	0.7953	17.29	18.54		
Average				93.5		17.32	18.52	1	

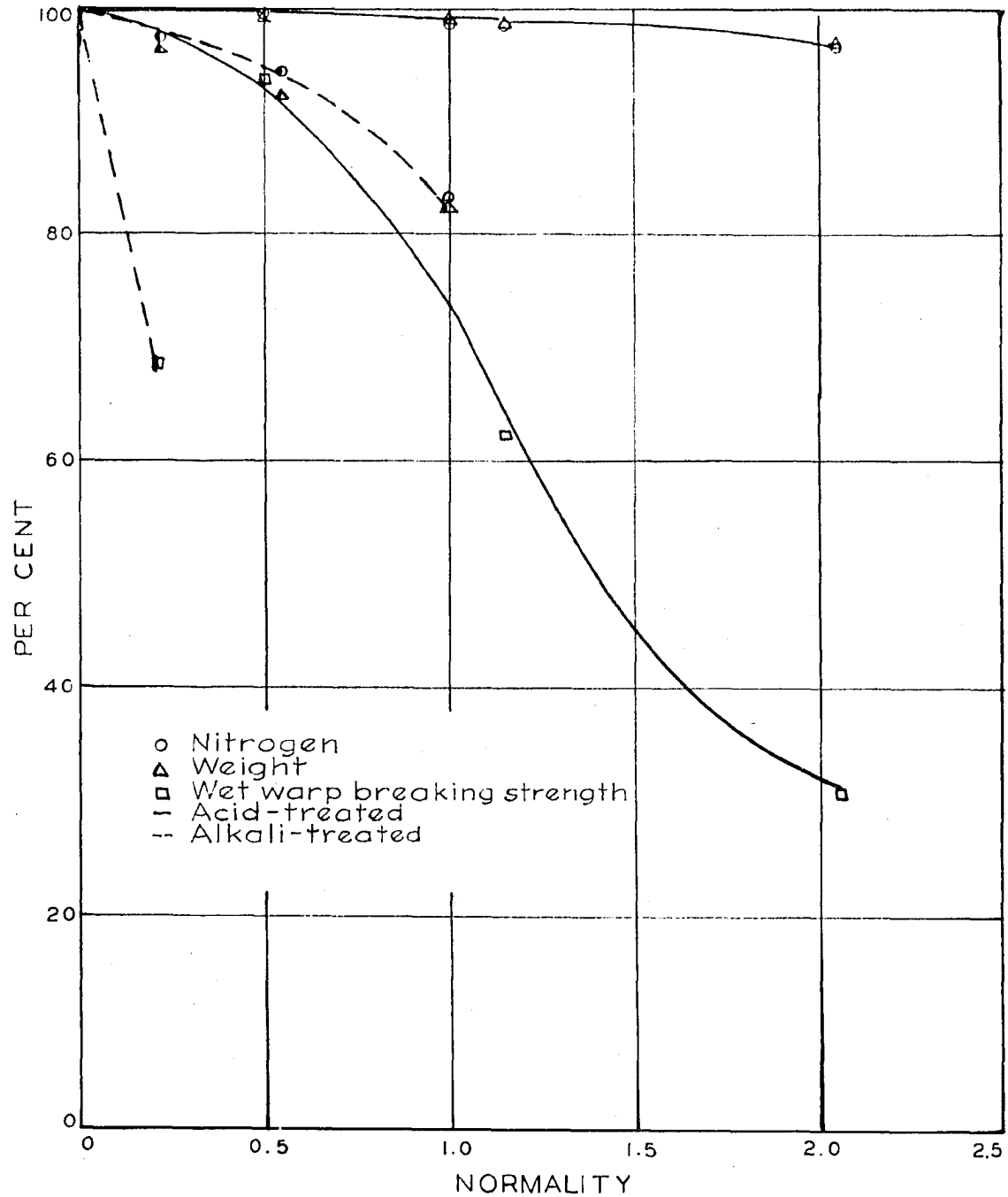


Figure V. Effect of hydrochloric acid and sodium hydroxide in ten hours at 40°C. on the weight, nitrogen, and wet warp breaking strength of wild silk fibroin.

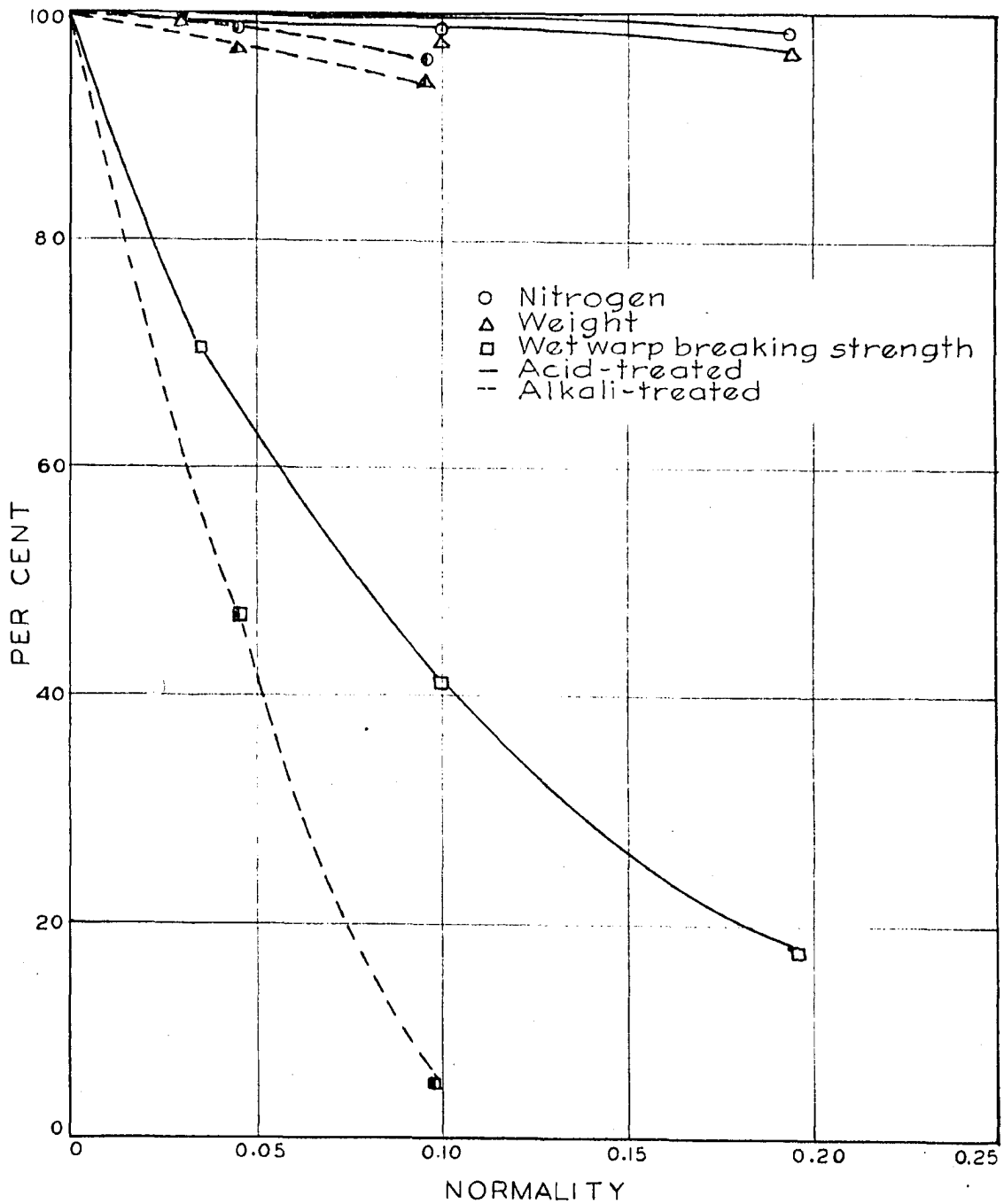


Figure VI. Effect of hydrochloric acid and sodium hydroxide in one hour at 100°C. on the weight, nitrogen, and wet warp breaking strength of wild silk fibroin.

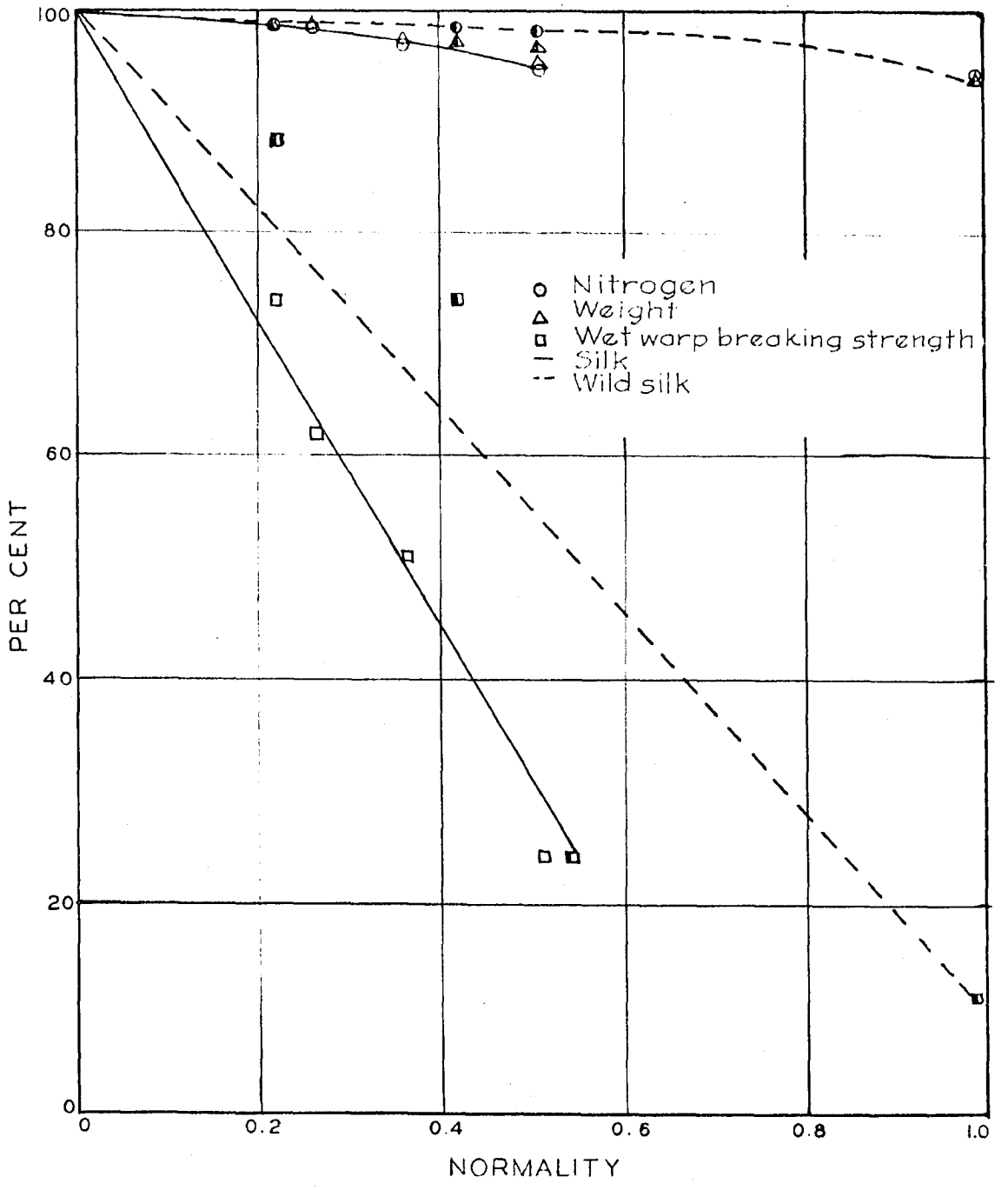


Figure VII. Effect of sodium hydroxide in ten hours at 25°C. on the weight, nitrogen, and wet warp breaking strength of silk and wild silk fibroin.

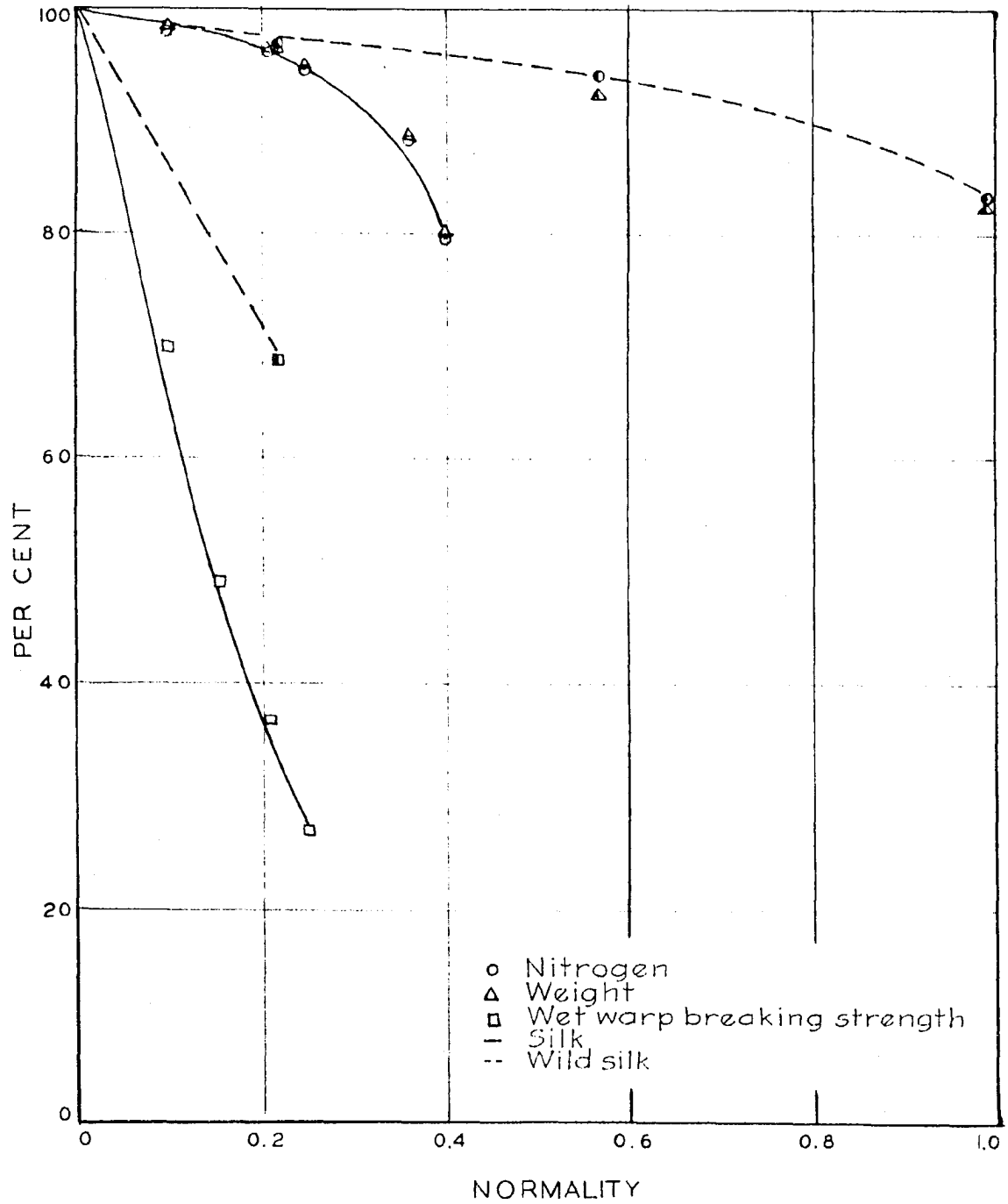


Figure VIII. Effect of sodium hydroxide in ten hours at 40°C. on the weight, nitrogen, and wet warp breaking strength of silk and wild silk fibroin.

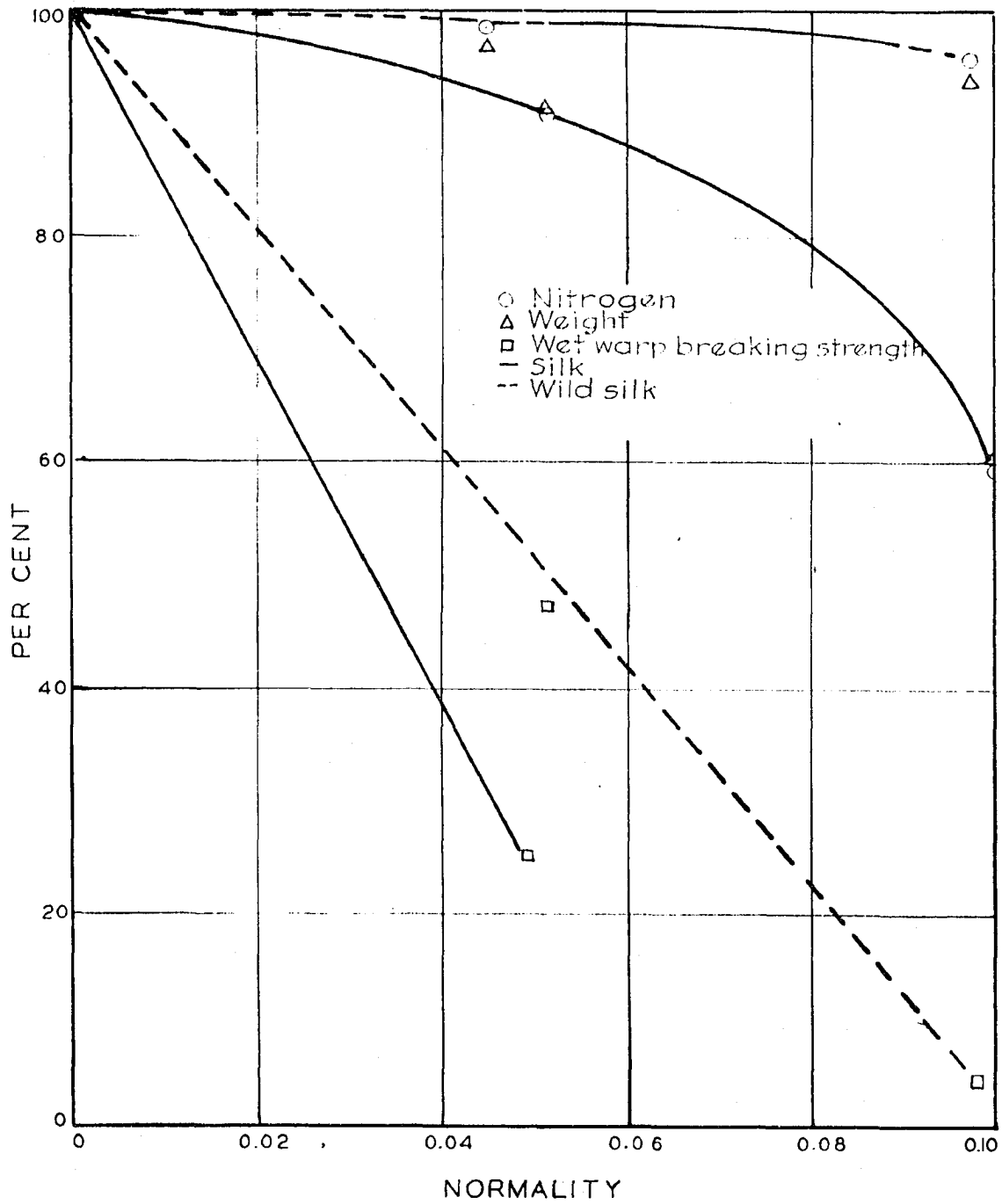


Figure IX. Effect of sodium hydroxide in one hour at 100°C. on the weight, nitrogen, and wet warp breaking strength of silk and wild silk fibroin.

Table 29

Effect of Concentrated Alkali on Fibroin

Time: 5 minutes
Temperature: 15°C.
Sodium hydroxide: 1.410 sp. gr.

Determination number	Fibroin	Treatment	Silk	Residue						
				Weight		Nitrogen			Breaking strength of wet warp	Elongation at breaking load
			gram	gram	per cent	gram	per cent of silk	per cent of residue	pound per inch	per cent
1	Silk	None	4.0626			0.7611	18.73			
2			4.2519			0.7960	18.72			
3			3.9994			0.7471	18.68			
4			4.1912			0.7817	18.65			
5			3.8814			0.7239	18.65			
6			4.1185			0.7711	18.69			
Average					100		18.69	18.69	44	29
1		Alkali	4.4371	4.4344	99.9	0.8286	18.68	18.69		
2			4.0349	4.0327	99.9	0.7490	18.56	18.57		
3			3.8451	3.8429	99.9	0.7118	18.51	18.52		
Average					99.9		18.58	18.59	34	23
1	Wild silk	None	4.3448			0.7950	18.30			
2			4.2063			0.7675	18.24			
3			4.0712			0.7400	18.18			
Average					100		18.24	18.24	16	23
1		Alkali	4.6028	4.5747	99.4	0.8387	18.22	18.33		
2			4.4380	4.4215	99.6	0.8085	18.22	18.33		
Average					99.5		18.22	18.33	11	16

Degradation of wild silk by dilute alkali has been shown to increase with increasing concentration of alkali. Weight and nitrogen of the residual fibroin have been found to decrease quite similarly, being logarithmic functions, $y = ax^b$, of the concentration of the hydrolytic agent. Increasing temperature also increased the degradation. Breaking strength and elongation at the breaking load have been shown to decrease more rapidly than weight or nitrogen.

Wild silk has been shown to resist decomposition by alkali better than silk fibroin. Contrary to the tendency observed with silk, alkaline hydrolysis of wild silk tends to leave a residue richer in nitrogen than the original fibroin, and richer in nitrogen than the residue from acid hydrolysis.

Concentrated alkali rendered fibroin transparent during the period of treatment, but its original appearance was restored upon washing; wild silk was not made transparent. There was no appreciable amount of shrinkage.

Degradation of Silk by Sodium Chloride

Preliminary tests were made by treating silk fibroin with 0.4977 N sodium chloride at 25°C. and 40°C. for ten hours. The samples were washed in distilled water until the rinse showed no opalescence with silver nitrate. Ten samples were hydrolyzed at each temperature; five were ashed at low red heat to determine the sodium chloride adsorbed on the silk, and five were weighed and analyzed for nitrogen. Table 30

shows the results of these tests.

To determine the deteriorating effect of sodium chloride dried in the silk for some time, samples were treated for ten hours at 40°C. with 0.1504 N, 0.2495 N, 0.3463 N, and 0.4977 N sodium chloride solutions, dried without rinsing or squeezing, and stored in paper envelopes under laboratory conditions for one year. After 365 days, these samples were washed free from chlorides, dried to constant weight, and analyzed for nitrogen. Breaking strength samples treated in the same way were broken wet immediately after washing. The results of these treatments are presented in Table 31.

Treatments for one hour at 100°C. were carried out with 0.0604 N and 0.7149 N sodium chloride, concentrations approximating those used in silk technology. Table 32 shows the results of these tests.

Table 30

Effect of Sodium Chloride on Silk Fibroin

Time: 10 hours

Determination number	Temperature °C.	Sodium chloride normality	Silk gram	Residue Weight gram	Weight per cent	Nitrogen gram	Nitrogen per cent	Ash gram	Ash per cent
1		Untreated	4.0626			0.7611	18.73		
2			4.2519			0.7960	18.72		
3			3.9994			0.7471	18.68		
4			4.1912			0.7817	18.65		
5			3.8814			0.7239	18.65		
6			4.1185			0.7711	18.67		
Average							18.69		
1			5.3457					0.0116	0.22
2			5.1672					0.0129	0.25
5			5.1957					0.0109	0.21
Average									0.23
1	25	0.4974	5.1449	5.1262	99.6	0.9606	18.67		
2			5.2343	5.2136	99.6	0.9762	18.65		
3			5.6539	5.6244	99.5	1.0564	18.68		
Average					99.6		18.67		
1			5.1190					0.0092	0.18
2			5.0702					0.0055	0.11
3			5.4407					0.0091	0.17
4			5.0837					0.0056	0.11
5			5.2316					0.0065	0.12
Average									0.14

Table 30, Cont'd.

1	40	0.4974	4.9681	4.9486	99.6	0.9224	18.57		
2			5.3569	5.3354	99.6	0.9873	18.43		
3			5.2116	5.1898	99.6	0.9634	18.49		
Average					99.6		18.50		
1			5.2688					0.0084	0.16
2			5.1148					0.0089	0.17
3			5.3720					0.0064	0.12
4			4.8437					0.0084	0.17
5			5.2946					0.0105	0.20
Average									0.16

Table 31

Effect of Sodium Chloride on Silk Fibroin after Long Standing

Time: 10 hours
Temperature: 40°C.

Determination number	Sodium chloride normality	Silk	Residue					
			Weight		Nitrogen		Breaking strength of wet warp pound per inch	Elongation at breaking load per cent
		gram	gram	per cent	gram	per cent		
1	0	4.3718	4.3545	99.6	0.8142	18.62		
2		5.1369	5.1098	99.5	0.9620	18.73		
3		5.6096	5.5793	99.5	1.0436	18.60		
Average				99.5		18.65	36	33
1	0.1504	5.2250	5.2086	99.7	0.9692	18.55		
2		4.9959	4.9714	99.5	0.9226	18.47		
3		5.3417	5.3204	99.6	0.9890	18.51		
Average				99.6		18.51	37	33
1	0.2495	5.5930	5.5791	99.7	1.0400	18.59		
2		5.1252	5.1082	99.7	0.9512	18.56		
3		5.2195	5.2034	99.7	0.9734	18.65		
Average				99.7		18.60		
1	0.3463	4.7029	4.6969	99.7	0.8768	18.62		
2		5.2263	5.2123	99.7	0.9683	18.53		
3		4.9321	4.9094	99.5	0.9193	18.64		
Average				99.6		18.60		
1	0.4977	5.2549	5.2232	99.8	0.9817	18.75		
2		5.3588	5.3364	99.6	1.0026	18.71		
3		4.7036	4.6900	99.7	0.8725	18.55		
Average				99.7		18.67	37	33

Table 32

Effect of Sodium Chloride on Silk Fibroin

Time: 1 hour
Temperature: 100°C.

Determination number	Sodium chloride normality	Silk	Residue					
			Weight		Nitrogen		Breaking strength of wet warp pound per inch	Elongation at breaking load per cent
		gram	gram	per cent	gram	per cent		
1	0	5.3240	5.3040	99.6	0.9890	18.58		
2		5.5804	5.5570	99.6	1.0326	18.50		
Average				99.6		18.54	42	28
1	0.0604	4.3322	4.3146	99.6	0.8043	18.57		
2		3.8894	3.8731	99.6	0.7162	18.41		
3		3.9855	3.9724	99.7	0.7423	18.63		
Average				99.6		18.54	44	28
1	0.7049	3.9743	3.9483	99.3	0.7341	18.47		
2		3.9047	3.8818	99.4	0.7220	18.49		
Average				99.4		18.48	42	28

Contrary to many statements recorded in the literature it was found that, under the conditions of experiment, sodium chloride had no appreciable effect upon silk fibroin, even when dried in the fabric for some time. No special effort was made to prepare an iron- or copper-free fibroin; in fact, this silk had been degummed in a steam-jacketed copper kettle. No discolored spots were noted after a year's storage of unrinsed silk and no change in mechanical failure or loss in weight or nitrogen occurred.

Degradation of Silk by Steam

Steaming was carried out in a high-pressure autoclave, equipped with an accurate steam-gauge and capable of withstanding over one hundred pounds. The silk samples were hung on glass rods placed across Pyrex beakers in such a way that no metal and no liquid which had flowed across metal could come in contact with the silk, which was protected from condensation from above by an inverted watch glass. The pressure was checked by reading a thermometer placed in a well level with the samples.

One series of tests was made by steaming the silk for one hour at 15, 30, 45, 60 and 75 pounds pressure, and a second series was made by steaming the silk for one-half, one, two, three, and five hours at 60 pounds pressure. The residual silk in each case was washed free of soluble decomposition

products by eight rinsings in distilled water. In cases of excessive tendering, the samples were washed on a filter to prevent loss of fibroin.

Tables 33 and 34 show the effect of increasing steam pressure upon silk and wild silk fibroin, while Tables 35 and 36 show the effect of increasing the time of steaming the two silks. Figures X and XI show degradation of silk and wild silk plotted against pressure and temperature, and Figure XII shows the effect of increasing the time of steaming.

Table 33

Effect of Steam on Silk Fibroin

Time: one hour

Determination	Steam pressure	Temperature	Sample	Residue					
				Weight		Nitrogen		Breaking strength of wet warp	Elongation at breaking load
number	pound	°C.	gram	gram	per cent	gram	per cent	pound per inch	per cent
1	0	100	4.0004	3.9902	99.7	0.7515	18.78		
2			3.7666	3.7631	99.9	0.7062	18.75		
3			4.0123	4.0019	99.7	0.7499	18.69		
4			3.9656	3.9603	99.9	0.7431	18.74		
Average					99.8		18.74	42	25
1	15	121.5	4.0184	4.0078	99.7	0.7512	18.69		
2			4.2562	4.2613	100.1	0.7954	18.69		
3			4.2037	4.1925	99.7	0.7840	18.65		
Average					99.8		18.68	42	24
1	30	134.5	4.0665	4.0465	99.5	0.7575	18.63		
2			4.1958	4.1760	99.5	0.7799	18.59		
3			3.7970	3.7671	99.2	0.7082	18.65		
4			4.2554	4.2371	99.6	0.7946	18.67		
Average					99.4		18.63	40	22
1	45	144.6	4.1702	4.1297	99.0	0.7773	18.64		
2			4.1630	4.1234	99.0	0.7765	18.65		
3			4.0536	4.0146	99.0	0.7540	18.60		
4			4.0247	3.9891	99.1	0.7482	18.59		
Average					99.0		18.62	30	16

Table 33, Cont'd

1	60	153	4.0459	3.9512	97.7	0.7442	18.39		
2			3.9847	3.9066	98.0	0.7343	18.43		
3			4.1304	4.0370	97.7	0.7597	18.39		
Average					97.8		18.40	24	13
1	75	160.5	3.9609	3.8106	96.2	0.7019	17.72		
2			4.5804	4.4229	96.6	0.8086	17.65		
3			3.9854	3.8399	96.3	0.7036	17.67		
Average					96.4		17.68	11	4

Table 34

Effect of Steam on Wild Silk Fibroin

Time: one hour

Determination number	Steam pressure pound	Temperature °C.	Sample Weight gram	Residue Weight gram	Residue Weight per cent	Residue Nitrogen gram	Residue Nitrogen per cent	Breaking strength of wet warp pound per inch	Elongation at breaking load per cent
1	0	100	3.8744	3.8666	99.8	0.7027	18.14		
2			4.0751	4.0523	99.4	0.7474	18.34		
3			4.1284	4.0976	99.2	0.7476	18.11		
4			4.3846	4.3666	99.6	0.7975	18.19		
Average					99.5		18.20	14	25
1	15	121.5	4.0039	3.9764	99.3	0.7280	18.18		
2			3.8658	3.8476	99.5	0.7029	18.18		
3			3.9843	3.9604	99.4	0.7244	18.18		
4			3.9207	3.8970	99.4	0.7157	18.25		
Average					99.4		18.20	12	15
1	30	134.5	3.8864	3.8549	98.7	0.7061	18.17		
2			4.8425	4.7738	98.6	0.8803	18.18		
3			4.6940	4.6369	98.8	0.8527	18.17		
Average					98.7		18.17	5	1
1	45	144.6	4.0187	3.9504	98.3	0.7267	18.08		
2			3.9628	3.8980	98.4	0.7182	18.12		
3			4.1118	4.0395	98.2	0.7423	18.05		
Average					98.3		18.08	< 1	

Table 34, Cont'd

1	60	153	4.1921	3.9918	95.2	0.7325	17.47	
2			4.5750	4.4130	96.5	0.8005	17.50	
3			4.0396	3.8591	95.5	0.7020	17.38	
Average					95.7		17.45	< 1
1	75	160.5	4.0147	3.6778	91.6	0.6811	16.97	
2			4.5054	4.2250	93.8	0.7620	16.91	
3			4.2055	3.9191	93.2	0.7075	16.82	
Average					92.9		16.90	< 1

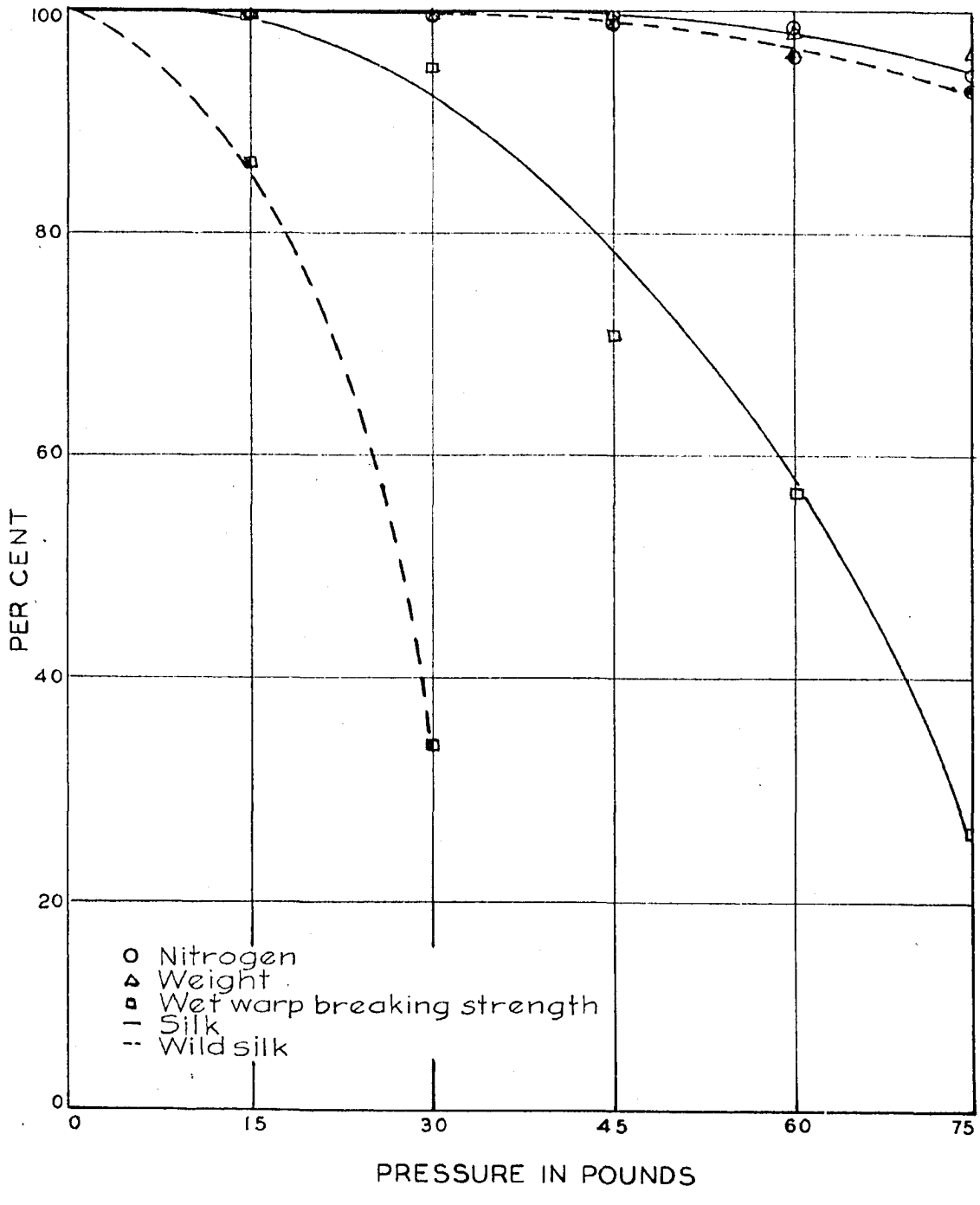


Figure X. Effect of steam for one hour upon the weight, nitrogen, and wet warp breaking strength of silk and wild silk fibroin.

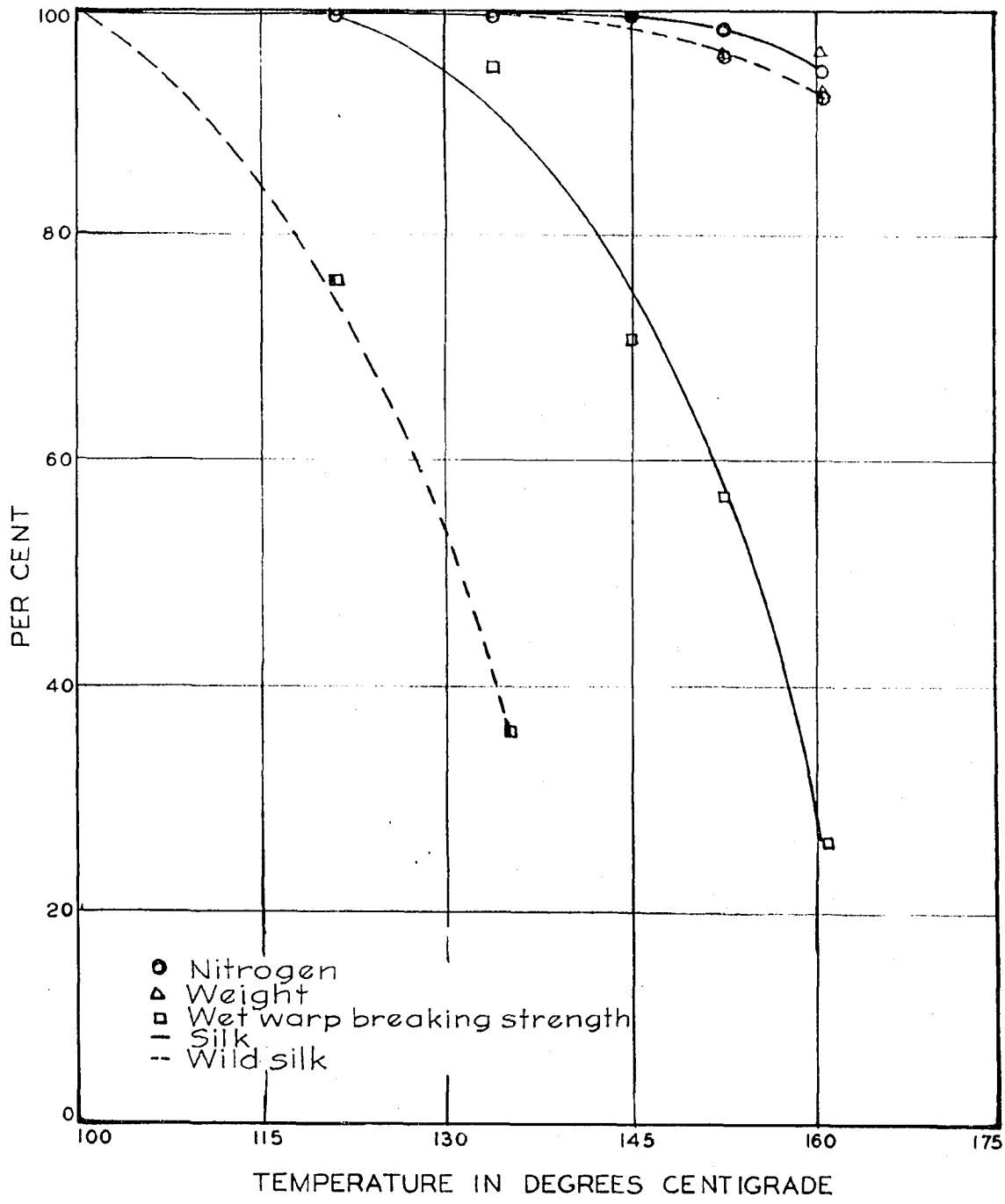


Figure XI. Effect of steaming for one hour at different temperatures upon the weight, nitrogen, and wet warp breaking strength of silk and wild silk fibroin.

Table 35

Effect of Time on Steaming Silk Fibroin

Steam pressure: 60 pounds
Temperature: 153°C.

Determination	Time	Silk	Residue Weight		Residue Nitrogen		Breaking strength of wet warp	Elongation at breaking load
number	hour	gram	gram	per cent	gram	per cent	pound per inch	per cent
1	0	4.1912			0.7817	18.65		
2		3.8814			0.7239	18.65		
3		3.9994			0.7471	18.68		
Average				100		18.66	42	33
1	1	4.0459	3.9512	97.7	0.7442	18.39		
2		3.9847	3.9066	98.0	0.7343	18.43		
3		4.1304	4.0370	97.7	0.7597	18.39		
Average				97.8		18.40	24	13
1	2	3.8920	3.7164	95.5	0.6994	17.97		
2		4.0261	3.8767	96.3	0.7269	18.05		
3		4.2209	4.0810	96.7	0.7658	18.17		
4		3.9160	3.7686	96.2	0.7095	18.12		
Average				96.2		18.08	12	7
1	3	3.9359	3.5896	91.2	0.6694	17.01		
2		4.0693	3.7155	91.3	0.6923	17.01		
Average				91.2		17.01	< 1	
1	5	4.1416	3.5131	84.8	0.6232	15.05		
2		3.9273	3.1540	80.3	0.5932	15.10		
3		3.9749	3.2066	80.7	0.6050	15.22		
Average				81.9		15.12	< 1	

Table 36

Effect of Time on Steaming Wild Silk Fibroin

Steam pressure: 60 pounds
Temperature: 153°C.

Determination	Time	Sample	Residue					
			Weight		Nitrogen		Breaking strength of wet warp	Elongation at breaking load
number	hour	gram	gram	per cent	gram	per cent	pound per inch	per cent
1	0	4.2063			0.7673	18.24		
2		4.0712			0.7400	18.18		
3		4.3448			0.7950	18.30		
Average				100		18.24	17	27
1	0.5	3.9958	3.9194	98.1	0.7269	18.19		
2		4.2075	4.1269	98.1	0.7537	17.91		
3		3.7697	3.7080	98.4	0.6775	17.97		
4		3.9548	3.8763	98.0	0.7197	18.20		
Average				98.1		18.07	1	
1	1	4.1921	3.9918	95.2	0.7325	17.47		
2		4.5750	4.4130	96.5	0.8005	17.50		
3		4.0396	3.8591	95.5	0.7020	17.38		
Average				95.7		17.45	1	
1	3	3.7857	3.2872	86.8	0.6020	15.90		
2		4.0676	3.5772	87.9	0.6539	16.08		
3		4.0172	3.5016	87.2	0.6410	15.96		
Average				87.3		15.98	1	
1	5	4.0536	3.0553	75.4	0.5603	13.82		
2		4.0980	3.1007	75.7	0.5684	13.87		
3		3.8287	2.9515	77.1	0.5272	13.77		
Average				76.1		13.82	1	

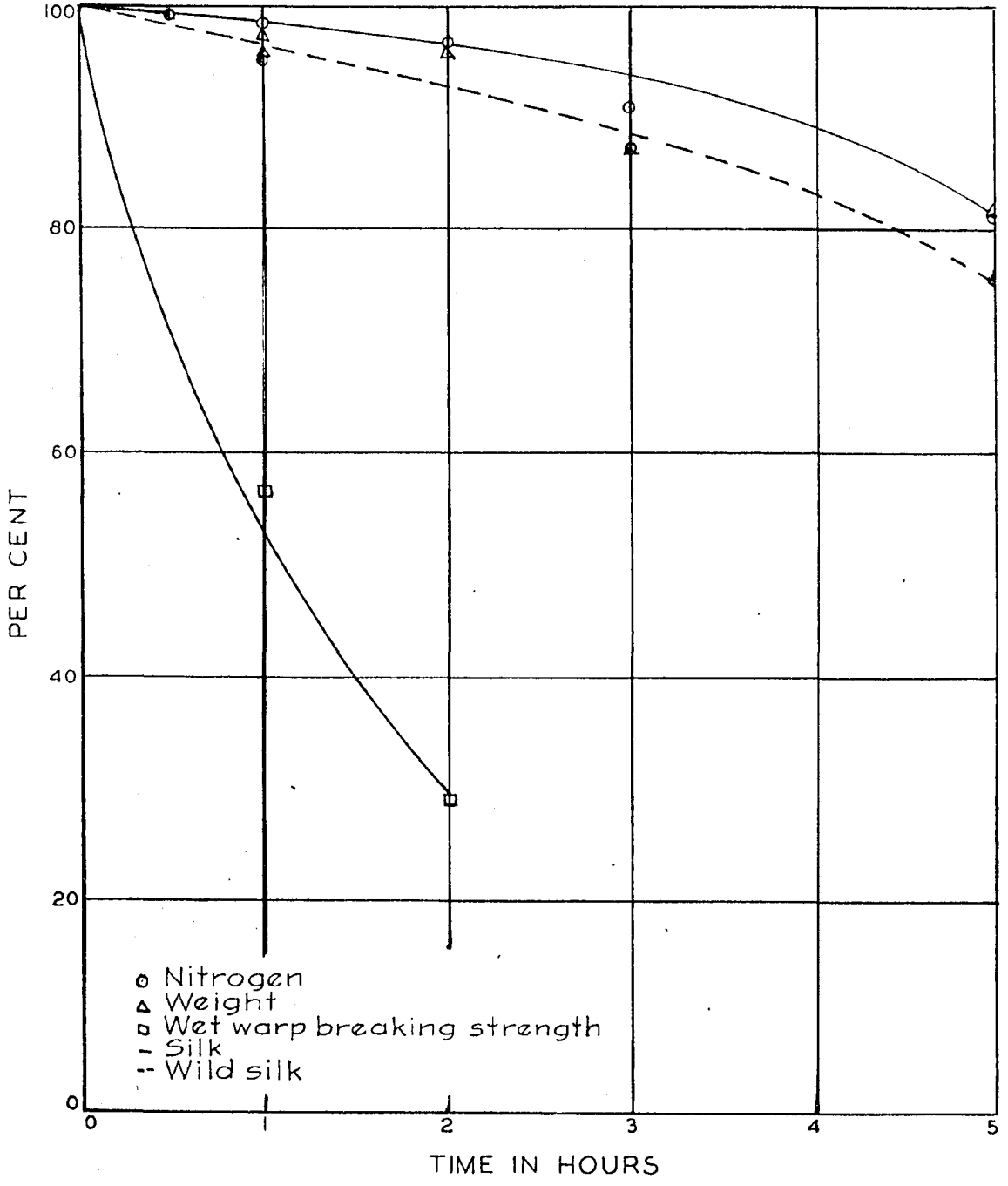


Figure XII. Effect of steam at sixty pounds pressure on the weight, nitrogen, and wet warp breaking strength of silk and wild silk fibroin.

Steaming of wild silk has been proven to be a questionable practice, although it has been shown that silk fibroin does not deteriorate appreciably upon very short steamings at sixty pounds pressure or upon steaming for an hour at fifteen pounds pressure.

It has been of interest to note that steaming is the one degradation studied which injured wild silk more than silk. It would appear that temperature was an important factor of this degradation, as the wild silk fabric decreased 25 per cent in wet breaking strength when subjected to a temperature of 100°C. in an oven for fifteen hours[+]. Anomalous results were obtained with mulberry silk Fabric I, which decreased by 30 per cent in wet breaking strength after the same treatment.

Steam has been observed to cause a darkening in color of both silk and wild silk fibroin, silk steamed for several hours at 60 pounds becoming very brown.

Weight and nitrogen of the residual fibroin from steaming have been shown to decrease quite similarly, as noted in the other degradations studied. Also, as in the other degradations, breaking strength and elongation have been shown to decrease much more rapidly than weight or nitrogen. Steam degradation of the silks was shown not to be an exponential function of the temperature or the pressure as acid and alka-

[+]Unpublished data obtained in this laboratory by Miss Mildred Barr.

line degradations were shown to be of concentration of the hydrolytic agent.

SUMMARY

1. Silk and wild silk fibroin have been oxidized for ten hours at 40°C. by 2.1800 N and 4.3601 N hydrogen peroxide, 0.2350 N hypochlorous acid, and 0.1973 N potassium permanganate in neutral solution. The degradation effected increased with increasing concentration, fibroin being more sensitive to oxidative degradation than wild silk fibroin. Degradation by potassium permanganate has been shown to be a linear function of the volume of reagent.
2. Silk and wild silk fibroin have been treated for ten hours at 40°C. with 0.1844 N sodium hydrosulfite in acetic acid solution. The slightly different values obtained for the fibroin after the treatment were within the limits of experimental error.
3. Wild silk fibroin has been subjected to hydrolysis for ten hours at 40°C. by 0.4977 N, 1.0263 N, 1.2264 N, and 2.1216 N hydrochloric acid, and for one hour at 100°C. by 0.0304 N, 0.1019 N, and 0.1950 N hydrochloric acid. The resulting degradation has been shown to increase with increasing concentration of acid, the weight and nitrogen of the residual fibroin being logarithmic functions, $y = ax^b$, of the concentration of the acid. Acid degradation of silk and

wild silk fibroin tends to leave a residue richer in nitrogen than the original fibroin. Wild silk has been shown much more stable than silk to degradation by acid. An increase in temperature has been shown to increase this degradation.

4. Silk and wild silk fibroin have been treated with hydrochloric acid, sp. gr. 1.145, at 15°C. for thirty seconds. Silk fibroin was much shrunk and gelatinized, although the appearance of wild silk was little affected.

5. Wild silk has been subjected to 0.3256 N, 0.4169 N, 0.5641 N, and 0.9863 N sodium hydroxide for ten hours at 25°C., to 0.2197 N, 0.5641 N, and 0.9863 N sodium hydroxide for ten hours at 40°C., and to 0.0452 N and 0.0969 N sodium hydroxide for one hour at 100°C. Degradation of wild silk by dilute alkali has been shown to increase with increasing concentration of hydrolytic agent, the weight and nitrogen of the residual fibroin being logarithmic functions, $y = ax^b$, of the concentration. Increasing temperature has been shown to increase this degradation. Wild silk has been shown to resist decomposition by alkali better than silk fibroin. Unlike the alkaline degradation of silk, alkaline degradation of wild silk tends to leave a residue richer in nitrogen than the original fibroin or the residue from acid degradation.

6. Silk and wild silk fibroin have been treated with sodium

hydroxide, sp. gr. 1.410, at 15°C. for five minutes. Fibroin became transparent during the period of treatment, but its original appearance was restored upon washing. Wild silk fibroin has been shown more resistant than silk fibroin to the action of concentrated alkali.

7. Silk fibroin subjected to 0.4977 N sodium chloride at 25°C. and 40°C. for ten hours has been shown unchanged. Silk fibroin treated for ten hours at 40°C. with 0.1504 N, 0.2495 N, 0.3463 N, and 0.4977 N sodium chloride and dried without rinsing for a year has been shown unchanged. Treatment for one hour at 100°C. with 0.0604 N and 0.7149 N sodium chloride caused no appreciable loss in weight, nitrogen, or mechanical failure.

8. Fabrics of silk and wild silk fibroin have been steamed for one hour at 15, 30, 45, 60, and 75 pounds pressure, and for one-half, one, two, three and five hours at 60 pounds pressure. The degradation has been shown to increase with increasing time or pressure. Wild silk fibroin has been shown much more sensitive than silk fibroin to degradation by steam.

9. Mechanical failure of silk and wild silk upon treatment with oxidizing agents, acid, alkali, or steam, has been shown more rapid than loss in weight or nitrogen, indicating a breakdown of fibrous structure preceeding formation of soluble decomposition products.

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[+]The abbreviations used are those of Chemical Abstracts except in cases where confusion might result.

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